CHEMISTRY

METHODS OF GAS ANALYSIS

Titrieranalytische
Methoden.

METHODS

OF

GAS ANALYSIS

BY

DR. WALTHER HEMPEL

PROFESSOR OF CHEMISTRY IN THE DRESDEN POLYTECHNICUM

TRANSLATED FROM THE SECOND GERMAN EDITION

BY

L. M. DENNIS

ASSISTANT PROFESSOR OF ANALYTICAL CHEMISTRY
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AUTHOR'S PREFACE

In publishing my "New Methods for the Analysis of Gases," it was not my intention to write a manual of gas analysis, but merely to describe my own researches and the construction of apparatus. My present plan, however, after ten years' experience and the most varied work with gases and their analysis, is to describe all of the operations which are involved in the analysis of gases with my apparatus. I have thought to give the book especial value by limiting myself to the description of those methods which, in my opinion, are at the present time the most practical. I have not endeavoured to give a complete description of all known methods, because the book would then become too bulky to be used as the laboratory guide, which it is intended to be.

The apparatus devised by Pettersson has been described, because a wholly new principle in the

measurement of gases is there brought into use. In the following pages I hope to give a guide to gas analysis by the help of which the various examinations, even the most difficult, can be carried out.

WALTHER HEMPEL.

DRESDEN, *December* 1889.

TRANSLATOR'S PREFACE

The rapidly growing recognition of the importance of gas analysis in the field of industrial as well as of pure chemistry, has made it seem probable that a translation of the latest work of so eminent an investigator in this line as Professor Hempel might prove acceptable to English-reading chemists. While preparing this English edition, the Translator was so fortunate as to enjoy throughout the progress of the work the personal co-operation of the author, and the changes that have been made were either suggested by Professor Hempel himself, or inserted with his approval. The chapter upon the determination of the heating-power of fuel has been largely rewritten, and new cuts of the latest forms of apparatus have been introduced in the place of those in the German edition. The chapter upon the analysis of illuminating gas has also been somewhat changed, and a new method for

the determination of the hydrocarbon vapours inserted. The other and less important alterations have been made in the desire to incorporate so far as possible the researches that have appeared since the publication of the German edition.

L. M. DENNIS.

ITHACA, NEW YORK,
November 1891.

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PART I

GENERAL METHODS

CHAPTER I

THE COLLECTING AND KEEPING OF GASES

In gas analysis, as in all other analytical work, the proper taking of the sample is one of the most important operations. Notwithstanding the rapid movement of gas molecules, currents of gases are often of varying composition, especially when chemical processes are simultaneously going on. On this account the place at which the samples of gas are taken is of the greatest significance. In pipes or other channels the point of smallest cross-section is the most suitable. In the examination of furnace gases it is best to take the sample at the point where the visible flame ends, because farther away, on account of the porosity of the wall, considerable quantities of air are always mixed with the gases from the fire. To take the sample, an iron tube is introduced into the furnace at a suitable point. A small lead pipe, such as is used for pneumatic bells, is attached to the outer end of the iron tube by means of a piece of rubber tubing. At temperatures under 300° the lead pipe itself may be inserted into the furnace. The great advantage possessed by such lead pipe is that it is very small

internally and can be manipulated as easily as rubber tubing. For very high temperatures either porcelain tubes or cooled iron tubes may be used. With acid gases glass tubes should be employed if possible.

Long rubber tubes must be avoided, but short pieces may safely be used for connections. Rubber receivers also are to be rejected. Vulcanised rubber acts towards gases as does a liquid, absorbing the gases and later, according to the prevailing pressure, giving them up again. For example, a piece of rubber tubing, 3 cm. long and from 4 to 5 mm. external diameter, absorbed 0·2 ccm. of carbon dioxide and 0·9 ccm. of nitrous oxide, and on lying in the air it gradually gave up these gases.

If the place where the gases are to be collected is directly accessible, as, for example, in the examination of mine-gases, the small "medicine bottles"[1] proposed by Bunsen may be used, the neck of the bottle being drawn out in the flame of the blast-lamp as in Fig. 1. Bunsen states[2] that the bottle should first be carefully heated between the shoulder and the neck, and the neck then drawn out by means of suitable tongs (Fig. 2). To fill the bottle with gas, the air in the bottle is sucked out through a small glass tube reaching to the bottom, this operation being repeated until the air originally in the bottle is completely replaced by gas from outside. Five or six full breaths are sufficient. It is self-evident that at each exhalation of the air sucked from the bottle, one must step aside

[1] These so-called medicine bottles are common glass bottles about 12 cm. high. They were recommended by Bunsen because they can be found almost everywhere, even small village drug-stores having a supply of them.

[2] Bunsen, *Gasometrische Methoden*, 2d ed. p. 12.

from the spot where the gas sample is being taken. The tightly stoppered bottle is then slightly warmed over a spirit lamp, and equilibrium between the expanded air inside the bottle and the outside atmosphere is re-established by lifting the cork for a moment. After cooling, the diminished pressure inside the bottle prevents the blowing-out of the glass when the narrow neck is fused together. The fusion may

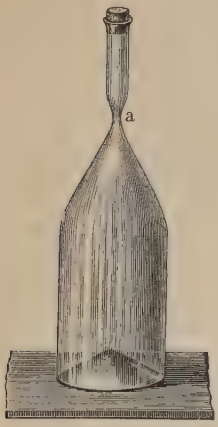

Fig. 1.

Fig. 2.

Fig. 3.

conveniently be performed with the blow-pipe shown in Fig. 3. The small lamp *a* holds about 3 grams of oil and is connected with the blow-pipe by means of a flexible wire that carries a collar *b* through which the tip of the blow-pipe is inserted.

The cork *c* serves as a mouth-piece by means of which the whole apparatus can be held and guided by the teeth alone. Thus both hands are left free, and the flame can still be moved in all directions, since

the relative positions of the blow-pipe tip and the lamp remain the same, however the instrument be held.

The arrangement used by the author in his parallel researches "upon the composition of the atmosphere at different parts of the earth" is also a very convenient one. The air was collected in glass tubes of the form shown in Fig. 4. *d* is about 4 mm. thick; *a*, *b*, and *c*, only 1 mm. These tubes were heated in an air-bath in the laboratory to 200°, and were then exhausted with the mercury air-pump and fused together at *c*.

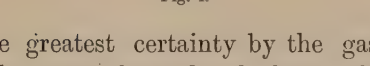

Fig. 4.

By simply breaking the tube at *b*, it is filled instantly and with the greatest certainty by the gas in question. The tubes are then closed for a few moments with a rubber cap, and are melted together at *a* over a candle. The exhausting with the air-pump has the advantage of rendering one less dependent upon the care of the person who fills the tubes. If, however, it is desired to avoid this exhausting, the tubes are given the following form (Fig. 5*a*). To fill such a tube, the gas to be examined is drawn through it and the tube is then fused together at *a* and *b* in a candle flame (Fig. 5*b*).

Such tubes can be most safely shipped by packing them in sawdust in boxes which have a separate compartment for each tube. The boxes themselves are placed in a larger box filled with hay.

The tube last described is filled by the displacement of the air already contained therein. Naturally it is here presupposed that large amounts of gas are at

one's disposal. If only a small quantity of gas is obtainable, the receiver must be filled with water or mercury, which is then displaced by the gas. Water can be used only when it is first saturated with the gases in question, as, for example, is always the case with the water of bubbling springs.

Fig. 5*a*.

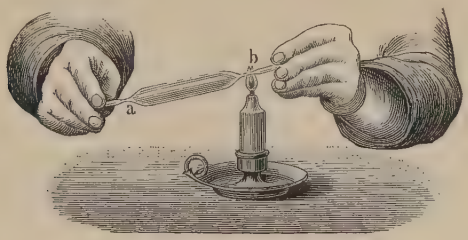

Fig. 5*b*.

To collect gas from such springs as are directly accessible, the small apparatus proposed by Bunsen[1] is used (Fig. 6).

This consists of a test-tube *c* of from 40 to 60 ccm. capacity, drawn out at *a* before the blast-lamp to the size of a fine straw, and connected air-tight with the funnel *b* by means of a well-fitting cork or a piece of vulcanised rubber tubing. Instead of the test-tube a small long-necked medicine bottle may be used, this being drawn out in the middle of the neck to a similar straw-like contraction. The apparatus is then filled with the water of the spring. This cannot be done without access of air, which would change the composition of the gases diffused through the spring water in

[1] Bunsen, *Gasometrische Methoden*, 2d ed. p. 2.

the tube. Hence the inverted apparatus, with the mouth of the funnel upward, is lowered below the level of the spring, and, with a narrow tube reaching to the bottom of the test-tube, the water which in the first filling had come in contact with the air is sucked out until one is satisfied that it has been entirely replaced by other water from the spring. If now the gas of the spring is allowed to rise through the funnel into the test-tube thus filled, the purity of the sample is assured. If the rising bubbles stop in the neck of the funnel or at the contraction *a*, they can easily be made to ascend by tapping the edge of the funnel upon some hard substance. The apparatus is then placed in a small dish and removed from the spring, and the tube is melted together at *a*. This can easily be done with the blow-pipe, the moisture at the point *a* having first been driven away by warming.

Fig. 6.

For the determination of the volume and composition of the absorbed gases in liquids, the Tiemann and Preusse modification of Reichardt's apparatus[1] can be recommended (Fig. 7).

This consists of two flasks *A* and *B*, each of about one litre capacity, and connected by tubes with the gas-collector *C*. The flask *A* is fitted with a perforated

[1] *Berichte der deutschen chem. Gesellschaft*, 1879, p. 1768.

rubber stopper in which is inserted the glass tube *a* bent at a right angle and ending flush with the lower surface of the stopper. *a* is joined by a piece of rubber tubing to the tube *bc*, which in turn connects with the gas-collector *C*. *C* is held by a clamp, has a diameter of 35 mm., is about 300 mm. long, and at the upper end is drawn out to a short, narrow, and slightly bent tube which can be closed with the rubber tube

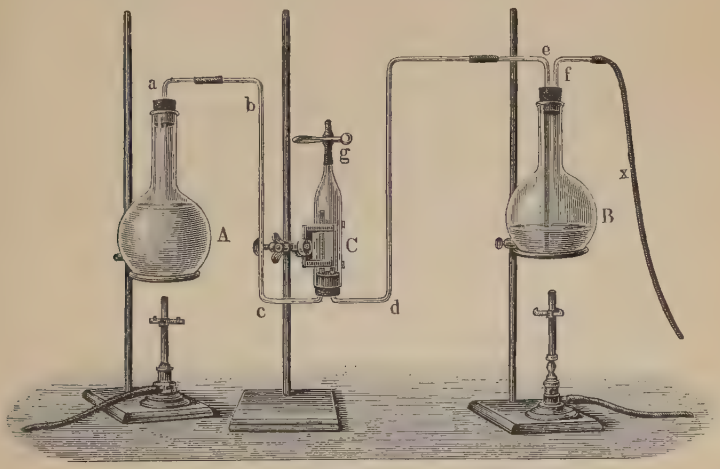

Fig. 7.

and pinchcock *g*. In the lower end of *C* is a rubber stopper with two holes through one of which the tube *bc*, projecting about 80 mm. into *C*, is inserted. Through the other opening passes the tube *d* which extends only slightly beyond the stopper and connects *C* with the flask *B*. *B* has a double-bore rubber stopper carrying the tubes *e* and *f*. *e* ends about 10 mm. above the bottom of the flask, and above the stopper it

is bent at a right angle and is connected with *d*. The tube *f*, which need not project below the stopper, carries a thin rubber tube *x* about 1 metre in length and provided with a mouth-piece. A pinchcock for closing the rubber tube between *a* and *b* is also needed.

The apparatus thus arranged is made ready for a determination by filling the flask *B* somewhat more than half full of boiled water and removing the flask *A* by slipping the tube *a* out of the rubber connection; then, by blowing into the rubber tube *x*, water is driven over from the flask *B* into the gas-collector *C* and the adjoining tubes, until the air is wholly displaced. The rubber tubes at *b* and *g* are now closed with pinchcocks. The flask *A* is then filled to the brim with distilled water, the stopper is inserted, water being thereby driven into the tube *a*, and the flask is again connected with *b*, the pinchcock being opened.

The water in *B* is now heated to gentle boiling, and that in *A* is allowed to boil somewhat more rapidly. The absorbed air is thus driven out, and the gases dissolved in the water which is in *A* and *C* collect in the upper part of *C*, from which they are removed by occasionally opening the pinchcock at *g* and blowing into the rubber tube *x*.

When, upon cooling the apparatus, the gases which have collected disappear, the heating of the flask *A* is discontinued, the pinchcock between *a* and *b* is closed, and *A* is disconnected and emptied. The water in *C* and *B* is now entirely free from absorbed gases, and air cannot enter from without because the liquid in *B* is kept continually boiling. The apparatus is now ready for a determination, which is made as follows :—

The cooled flask *A*, whose capacity has been previously determined, is filled with the water to be examined, and the stopper is pressed in so far that the air in the tube *a* is completely driven out. *a* is then connected with *b*, care being taken that in so doing no air-bubbles are enclosed. The pinchcock between *a* and *b* is opened and the water in *A* is heated to gentle boiling. The dissolved gases are hereby driven over into the gas-collector *C*. Steam is formed at the same time. The heating of the flask *A* must now be so regulated that the gas and steam evolved never drive out more than half the liquid in *C*: otherwise there is danger of gas-bubbles entering the tubes *d* and *e* and thus escaping.

After heating for about twenty minutes, the flame under *A* is removed. In a few minutes the steam in *A* and *C* condenses, and water passes from *B* towards *C* and *A*. If a gas-bubble is observed in *A*, the flask *A* must again be heated and cooled in the manner just described. The operation is ended when the hot liquid flows back and completely fills *A*. The rubber tube *g* is then connected with a small tube which is filled with water or mercury, and the gas standing over the hot liquid in *C* is driven over into a eudiometer, gas burette, or gasometer by blowing into the tube *x* and opening the pinchcock *g*.

Gases are set free in many chemical reactions that take place in sealed tubes. If one wishes to examine these gases, Bunsen directs [1] that when the tube is fused together, it be drawn out to a fine tip about 2 mm. wide and 50 mm. long. To collect the gases given off, a mark is made at *a* with a sharp file, and

[1] Bunsen, *Gasometrische Methoden*, 2d ed. p. 10.

the tip is connected with a capillary glass tube by means of a short piece of rubber tubing (Fig. 8).

For safety's sake wire ligatures are put on at *b* and *c*. On breaking the tube inside the rubber at *a*, the gas passes through the delivery tube and can be collected in any desired receiver. If very strong pressure in the tube is to be expected, the rubber

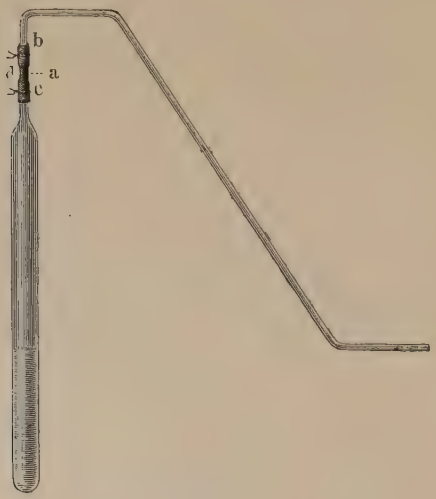

Fig. 8.

connection is surrounded with a strip of linen, and the tube itself is wrapped in a cloth. A third ligature put on at *d* makes it possible to stop the escape of gas at any time, the rubber forming with the broken-off glass tube a Bunsen rubber stopcock.

The taking of the gas sample is especially difficult when at the same time the disturbing influences of elevated temperature, chemical action, and high me-

chanical pressure must be overcome, as for example in the collecting of gases from the blast-furnace. Bunsen and Playfair, in their investigation at the blast-furnace in Alfreton, England, introduced a wrought-iron tube into the throat of the furnace and allowed it to sink with the charge. The tube consisted of five pieces, which were screwed on from time to time as the tube sank.

Winkler has proposed[1] the device shown in Fig. 9, the form here given being that used by Schertel in his investigations on the Freiberg lead furnaces. They both used three tubes, which could be lengthened as much as desired by screwing on additional pieces. The bottom of the outer tube is welded on, and into it the two inner tubes are tightly screwed; *b* has a number of side openings just above its lower end, but it does not pass through the bottom, whereas *a* does. When in use, a stream of water enters at *b* and, passing into *A*, surrounds the tube *a* and protects it from the action of the heat. The water is led off at *c* by a rubber tube. The stoppage of the tube by dust is prevented by putting a wad of asbestos into the mouth of the tube *a* while the apparatus is being introduced into the furnace. The tube is let down by a pulley to the lowest point at which the gas is to

Fig. 9

[1] Clemens Winkler, *Anleitung zur chemischen Untersuchung der Industrie-Gase*, Part II. p. 7.

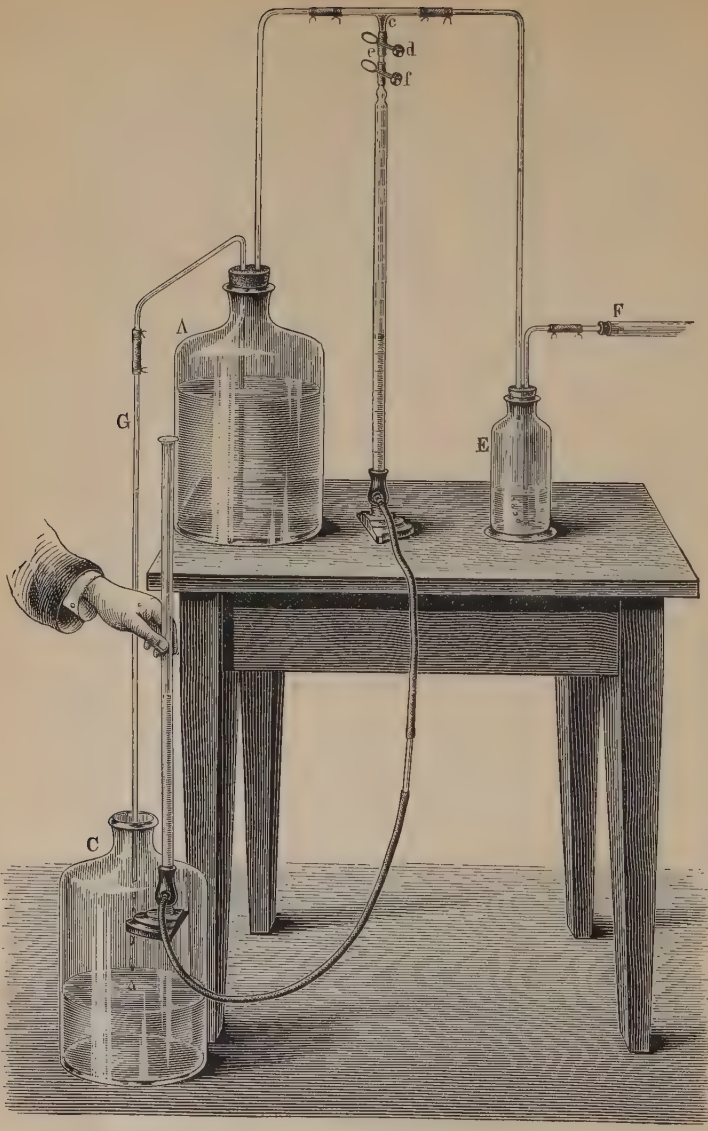

Fig. 10.

be taken. The asbestos stopper is then pushed out with a thick iron wire. To take samples of gas from points higher up, the tube is simply drawn up the desired distance.

If the gases to be collected have a pressure less than the prevailing atmospheric pressure, an aspirator must be used. The simplest form consists of two interchangeable bottles of equal size and the same width of neck. Fig. 10 shows an arrangement which may be used when one wishes to take samples at the same time in a gas burette (see p. 22). The water passes from the bottle *A* through the siphon *G* into *C*, and thereby draws the gas from the tube *F*. When *A* is empty, *C* which is now full is put in its place, the aspirating of the gas continuing as long as the samples are being taken.

Small rubber pumps are also very convenient

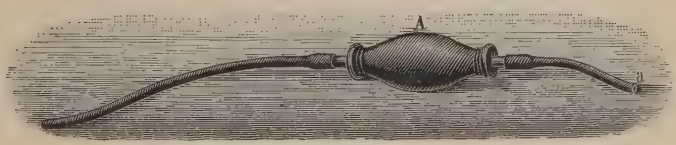

Fig. 11.

(Fig. 11). These act both as suction and pressure pumps. The thick-walled bulb *A* is supplied with two simple valves working opposite to each other. When the bulb is compressed with the hand, pressure is produced in one of the tubes, and when the bulb, through the elasticity of the rubber, assumes its original form, suction on the other side results. Either rubber valves or metallic plug-valves are used; the latter have the advantage of retaining their

efficiency for many years. It must not be forgotten that gas mixtures are affected by the rubber, and that on this account the apparatus for receiving the gas must be put before the pump.

When running water is at hand, an aspirator may

Fig. 12.

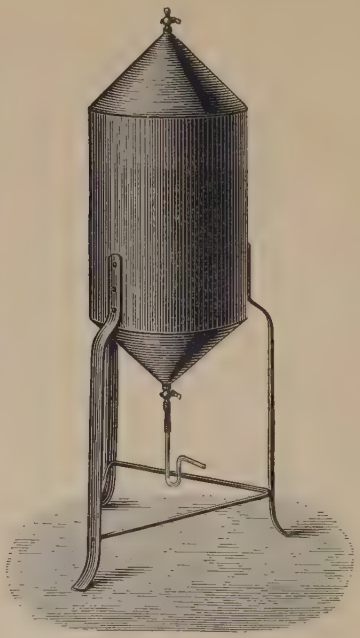

Fig. 13.

be used with advantage. The form proposed by Finkener is one of the simplest (Fig. 12). In this the water passes under high pressure from the narrow tube *a* into the wider tube *c*, and acts as an injector, thus sucking air in at *b*.

With such an apparatus as that constructed by Körting,[1] steam may also be used for aspirating.

An aspirator of sheet zinc is well suited to the collecting and keeping of large quantities of gas. It consists of a large cylindrical vessel whose conical ends are closed air-tight by stopcocks (Fig. 13).

A gas can be best kept in the fused glass tubes already described, but glass bulbs supplied with two glass stopcocks are also quite satisfactory (Fig. 14).

Fig. 14.

Metallic receivers should be used for analytical purposes only when the gas is to remain in them but a short time. They are, however, not easily broken, and are especially well adapted to the transport of large quantities of gas.

Rubber sacks should never be employed, since gas mixtures confined in them rapidly change in composition.

If large amounts of gas are to be collected and kept for analysis for a considerable length of time, the portions of gas taken for analysis must be displaced with mercury. It is utterly impracticable to use water for this purpose, for continual changes would take place, since the absorption varies with the pressure and temperature. A gasometer which for years past has given good satisfaction in the Dresden laboratory is shown in Fig. 15. The large glass bulb *A* serves to hold the gas. At the top it carries the bent capillary tube *a*, and at the bottom it is joined to the level-bulb *B* by a rubber tube. The capillary is

[1] Gebr. Körting, Hanover, Germany.

closed by a rubber tube and pinchcock. The apparatus is first filled with mercury. By lowering or raising the level-bulb, gas can be drawn in or driven out as desired. If gases are to be kept for some time,

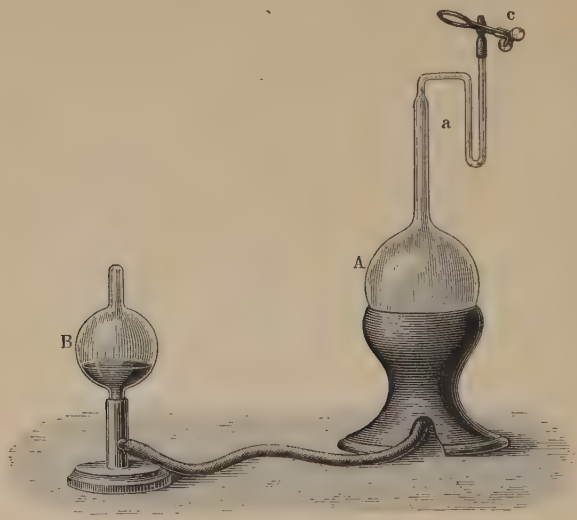

Fig. 15.

the capillary tube *a* is filled with mercury by means of a little pipette inserted at *c*. This closes the bulb perfectly. In such an apparatus gases may be kept unchanged for an unlimited time.

Fig. 16.

Small glass bulbs (Fig. 16) are also very convenient. They are filled with gas in a mercury trough, and are then placed mouth downwards in small porcelain crucibles containing mercury. The gas is taken out with the gas pipette to be described later.

CHAPTER II

THE ANALYSIS OF GASES

For the analysis itself various methods, corresponding to the nature of the gases, suggest themselves. The gases may be separated—

1. By successive absorption of the different constituents and the volumetric determination of each.

2. By absorption and subsequent determination by titration or weighing.

3. By combustion and the volumetric or gravimetric determination of the products.

Under all circumstances, however, the first operation is the measuring of the gas.

General Remarks on the Measuring of Gases.

From the nature of a gas it is clear that its quantity can generally be better determined by measuring its volume than by ascertaining its weight. Hence one of the most important operations in gas analysis is the measurement of gases.

The volume of a gas is influenced by pressure, temperature, and the tension of the liquid present.

By Boyle's law the density and the pressure of a gas are proportional to each other.

According to Gay-Lussac's law gases expand $\frac{1}{273}$ of their volume at 0° for each degree of temperature.

The tension of the confining or absorption liquid causes an increase of volume. This increase is dependent upon the temperature, is independent of the pressure, and varies with the chemical nature of the liquid in question.

To reduce a gas volume, measured in a moist condition, to the volume which it would occupy in a dry state at 0° C. and 760 mm. pressure, the following formula is used: b is the observed barometric pressure, t the temperature, e the maximum tension of aqueous vapour at this temperature, and V the observed volume:—

$$V_o = V \frac{b - e}{760(1 + 0{\cdot}00367t)}.$$

In very exact work corrections may also be introduced for the expansion of the mercury and glass of the barometer.

Only those volumes can be directly compared with one another that have been reduced to equal pressure and temperature, the tension of the liquid being also allowed for.

Parallel gas measurement can be carried on under—

1. Varying pressure, varying temperature, and varying volume.

2. Constant pressure, constant temperature, and varying volume.

3. Constant temperature, varying pressure, and constant volume.

4. Constant pressure, varying temperature, and varying volume.

In the first case the gas volumes found must be reduced to like temperature and pressure. In the second and third the resulting volumes can be directly compared, since density and pressure are directly proportional.

Apparatus for Technical Gas Analysis.

Gas Burettes.

A. The Simple Gas Burette (Fig. 17).

This consists of two glass tubes, *a* and *b*, which are set in iron feet and are connected by a thin rubber tube about 120 cm. long. To facilitate the cleaning of the burette the rubber tube is divided in the middle and the two ends joined by a piece of glass tubing.

Inside the feet the tubes *a* and *b* are bent at right angles and conically drawn out. The end projecting from the iron is of about 4 mm. external diameter and is somewhat corrugated, so that a rubber tube may be tightly fastened to it by wire ligatures.

The measuring tube *b* ends at the top in a thick-walled tube *c* of from $\frac{1}{2}$ to 1 mm. internal diameter and about 3 cm. long. Over this a short piece of new black rubber tubing is wired on. The rubber tube is closed, in a completely satisfactory manner, by a Mohr pinchcock, which is put on close to the end of

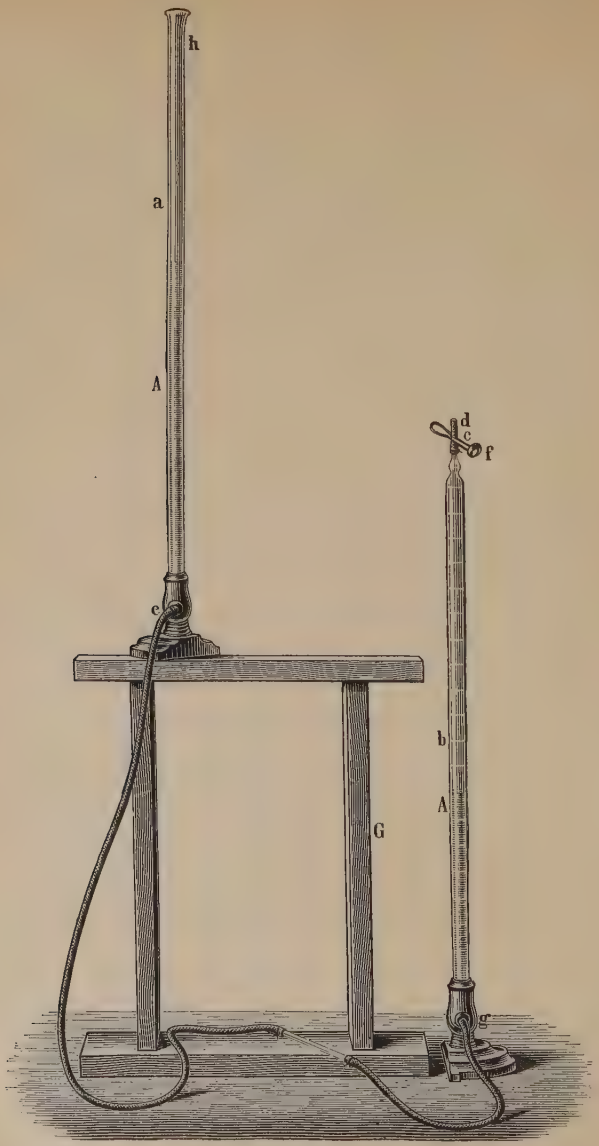

Fig. 17.

the capillary. The author at first closed the burette with a glass stopcock, but by experience he found it to be much easier to make tight rubber taps and connections than perfectly tight glass stopcocks, wholly aside from the fact that by giving up the glass cock the apparatus is rendered less fragile and less costly.

Further, as will be seen from the description of the *complete* analysis, the rubber connections come in contact either with none of, or with only so very small quantities of the absorbent, that it need not be feared that the rubber will become slippery and slide off from the glass tube. The author would here call especial attention to the fact that, whether glass stopcocks or pieces of rubber tubing are used, they must without fail be tested from time to time to see if they are tight. The pinchcock is always taken off from the rubber tube after using, this helping much to keep the latter in good condition. Notwithstanding the fact that readings cannot be made under the rubber tube, and that the pinchcock cannot always be put on above the tube in exactly the same position, no error results therefrom, since the glass tube *c* is very small. The author has found that the differences in volume are much less than a tenth of a cubic centimetre, a variation which, in determinations not made over mercury, may be entirely disregarded. The graduated measuring tube *b* contains 100 ccm., the lowest mark being slightly above the iron foot. The cubic centimetres are divided into fifths, and the numbers run both up and down. The tube *a*, which we will call the level-tube, is somewhat widened at the upper end *h* to facilitate the pouring in of liquids.

With the simple gas burette alone an analysis may

be made of a gas mixture not too soluble in water, and the author used it with good success before devising the apparatus to be mentioned later. For these reasons the manipulation by means of which it is possible to carry out an analysis with this simplest form of burette will be described.

Manipulation of the Gas Burette.

Fill the tubes *a* and *b* with water, taking care to drive all air out of the connecting rubber tube by suitably raising or lowering the tubes; then join the burette to the vessel containing the gas by means of a glass or rubber tube filled with water. (This connecting tube can be easily filled with water by raising the level-tube.)

To fill the burette with the gas to be examined, grasp the tube *a* in the left hand, close the rubber tube at *c* by pressing it between the little finger and the palm of the hand, and pour out the water in *a*.

Place the level-tube on the floor and open the pinchcock *f*. The water will now flow into the level-tube and the gas will be drawn into the burette. When *b* is filled with the gas, close the pinchcock *f*, disconnect *b* from the gas-holder, and after the liquid has run down from the walls of the burette, take up the tubes by the iron feet and by raising or lowering bring the water in the tube to the same level. The gas is now under atmospheric pressure, and its volume is read off. To measure off exactly 100 ccm., bring somewhat more than 100 ccm. of the gas into the burette, close the latter with the pinchcock, and let the water run down. Now compress the gas to less than

100 ccm. by raising the level-tube, close the rubber tube at *g* with the thumb and first finger of the left hand, set the level-tube on the table, and raising the burette in the right hand to the level of the eyes, carefully open the rubber tube and let the water run back until the meniscus stands at the 100 ccm. mark. Keeping the rubber tube still compressed, open the pinchcock for a moment; the excess of gas will escape, and there remains in the burette exactly 100 ccm. of gas under atmospheric pressure.

To bring as much as possible of the absorbent into the burette, lower the level-tube until the expanded gas begins to enter the rubber tube, compress the tube at *e* as before described, and pour the water out of *a*. The absorbing liquid is now poured into *a*, and the tube raised as far as the rubber tube permits; in this way a considerable amount of the reagent, diluted with the water in the rubber tube, is brought into the burette.

Compressing the tube at *g*, bring the gas into thorough contact with the absorbent by vigorously shaking the burette. When no further decrease of the volume of the enclosed gas takes place, the reading is made as before described. The difference in volume gives the amount of the absorbed gas.

The advantages of this simple burette over the other similar forms with which the author is acquainted, are the following:—

1. Easier and quicker manipulation, since both tubes may be freely moved, and since the adjusting of the levels does not take place through narrow stop-cocks, but on the contrary can be instantly done by raising or lowering the tube.

2. The possibility of bringing the gas under very different pressures by raising or lowering one of the tubes, thus rendering it easy, from the beginning of the analysis, to bring the gas into contact with large amounts of the absorbent.

3. The simple glass tubes can be more easily cleaned, are less liable to be broken, and are cheaper.

In the analysis of gases which are very soluble in water (among these may be classed carbon dioxide except when it is present in very small amounts, as is the case in illuminating gas and some furnace gases), the measurement of the initial volume cannot be made over water, nor over water saturated with the gases. In this case one must use a gas burette which, since it is a modification of the Winkler apparatus, we will call the modified Winkler gas burette.

B. The Modified Winkler Gas Burette (Fig. 18).

This consists of the level-tube *a* and the measuring tube *b* connected by a thin rubber tube about 120 cm. long and fastened into iron feet. *b* is a glass tube of about 100 ccm. capacity, provided with the three-way cock *c* and the simple glass stopcock *d*. The space between the two stopcocks is divided into exactly 100 equal parts, and each part into fifths. The thick-walled tube *e* must have an internal diameter of from only $\frac{1}{2}$ to 1 mm., so that bubbles of the gases which are passed in and out cannot stop in the tube.

Instead of the glass stopcock *d* a rubber tube and pinchcock may be used as with the simple burette.

Before filling the burette with the easily soluble gases, the tube *b* is first dried by rinsing it out with

a few cubic centimetres of absolute alcohol and then with ether, the latter being driven out by aspirating through the tube the gas to be analysed. To do this, join the end *e* of the burette by means of a rubber tube, or better a glass tube, to the vessel containing the gas and bring the three-way cock into such a position that its longitudinal opening communicates with the inside of the burette. Connect the cock with the aspirator. After the gas has been drawn through for a time, close the lower and the upper stopcocks. The gas, if under pressure, is brought to atmospheric pressure by momentarily opening the upper stopcock. The remainder of the apparatus is now filled with water run in through the three-way cock, which is so

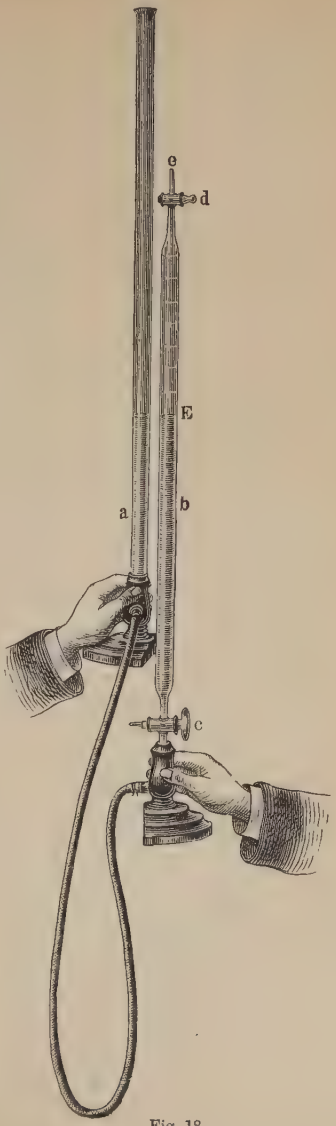

Fig. 18.

turned that it communicates with the rubber tube. The water must previously be saturated with those constituents of the gas mixture which are slightly soluble in water. If the mixture contains very soluble gases, *a* and *b* are connected by bringing *c* into the proper position, and the gases are absorbed directly in the burette by shaking them with the water therein. When a mixture contains easily soluble gases, they may be absorbed with water and then determined in the solution by titration. In the analysis of very soluble gases, it is preferable, except in a few rare exceptions, to lead large quantities of the gas mixture through suitable apparatus containing known amounts of the absorbents, and to determine the quantity of the unused reagent by titration.

The absorbing liquids for determining the constituents which are only slightly soluble in water, are brought into the burette by means of a funnel connected with the longitudinal opening of the stopcock by a piece of rubber tubing.

Beyond this the manipulation is the same as with the simple gas burette.

C. The Gas Burette with Correction for Temperature and Pressure (Fig. 19).

The graduated measuring tube *A* contains 100 ccm. and is fastened into the heavy cast-iron foot *E*. The burette is closed at the top by a Greiner-Friedrichs stopcock, which opens into the two capillary tubes *a* and *b*. The burette is connected by two short pieces of rubber tubing with the manometer *F* and the Pettersson correction tube *B*. This correction tube is a

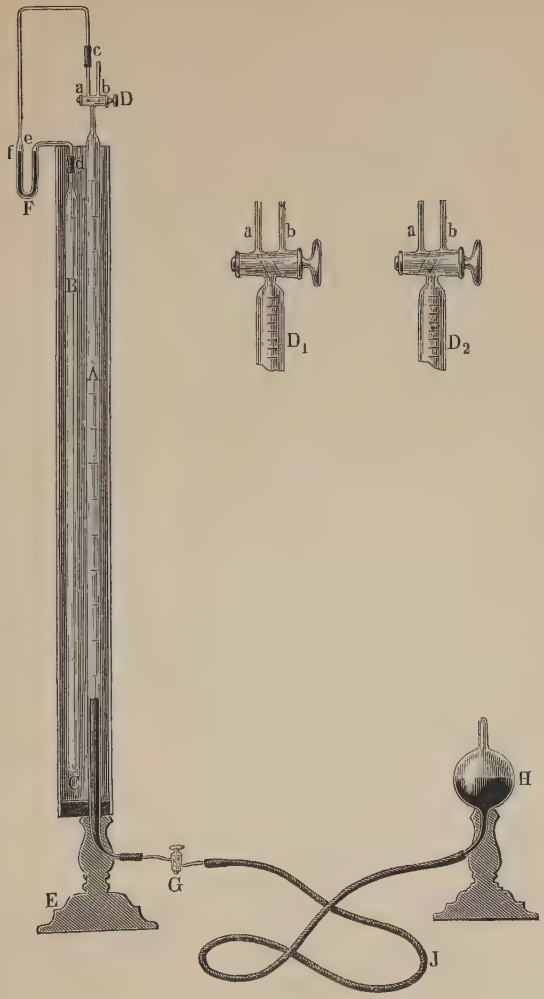

Fig. 19.

plain glass tube closed at the bottom and joined at d to the manometer F by a piece of rubber tubing. Both the burette and correction tube stand in a wide glass tube C filled with water. C is open at the top, and is closed at the bottom by a single-bore rubber stopper. The U-shaped part of the manometer tube F is about 6 mm. wide; from e to c it is capillary when mercury is used as the confining liquid, but when water is used this part is 3 mm. wide. The burette is connected by rubber tubing with the stop-cock G and the level-bulb H.

Mercury, or water saturated with the gas to be analysed, is used as confining liquid. If the gases are to be measured in a moist condition, as is generally advisable, a drop of water is introduced into the correction tube B.

Before using the apparatus for an analysis, the size of the space between f and c in the manometer tube must be determined once for all. This is done by drawing some air into the burette, and then bringing the three-way cock into the position D_1, so that the burette communicates with the manometer. By raising or lowering the level-bulb the enclosed gas can easily be brought to the pressure of the gas in the correction tube B. This is accomplished when the liquid stands at the same height in both sides of the U-tube of the manometer. The cock G is now closed, and the size of the gas volume is read off on the scale.

Upon again opening G and lowering the level-bulb, the liquid in the manometer tube may easily be drawn over as far as c; D is then closed again and another reading of the volume is taken, the gas being first

brought to the pressure of the atmosphere by raising the level-bulb. The difference of the two readings gives the capacity of the tube between *f* and *c*. It is here presupposed that the air enclosed in *B* has the same pressure as the outside atmosphere. This can easily be brought about, for equilibrium is established by simply drawing the manometer tube at *d* out of the rubber connection.

Other slight changes of pressure need not be considered in making this measurement, since the volume of gas is itself very small.

This constant having been determined, the measurement of gases is made as follows :—

Fill the burette completely with confining liquid by raising the level-bulb, connect *b* by a capillary tube with the vessel containing the gas to be examined, and draw the gas into the burette. The stopcock must of course be in the position of D_2. To measure the gas, turn the cock into the position D_1, and by then raising or lowering the level-bulb bring the liquid in both sides of the manometer to the same level. The stopcock *G* is now closed, and the reading is taken. The true volume is equal to that read off plus the correction-constant. After measuring, draw the gas out of the manometer tube back into the burette.

The absorptions are made in gas pipettes (see p. 32), which are connected by means of capillary tubes with the tube *b*.

The apparatus may be made in one piece, but greater durability is ensured by using the rubber connections *c* and *d*. Since these rubber pieces are very short, and since the gas comes in contact with them

only when the measurement is made, they cause no error even in very exact analyses.

The oblique Greiner-Friedrichs glass stopcocks have the great advantage over ordinary stopcocks of preventing the formation of grooves and resulting leakage.

On account of the solubility of gases in water, the accuracy of the analysis made by direct absorption in a gas burette is not very great, and the applicability of the method is also limited by the fact that only those absorbents which do not rapidly attack rubber can be used. Further, the apparatus must be cleaned after each analysis, and the absorbing liquid must be frequently renewed.

These disadvantages disappear when the absorption is made in an especial apparatus—the gas pipette—as first suggested by Doyère. These gas pipettes contain the reagents, and their construction renders it possible to bring the gases into intimate contact with the absorbents. There must be as many of them as there are absorbable constituents in the gas mixture.

The following forms, varied to suit the nature of the different reagents, are used :—

Absorption Pipettes.

A. The Simple Absorption Pipette.

This is a modification of the Ettling gas pipette, first used by Doyère for the absorption of gases, and it is filled with such absorbing liquids as rapidly

attack rubber, *e.g.* fuming sulphuric acid, bromine, fuming nitric acid, etc. (see Part II.)

It consists of two large bulbs, *a* and *b* (Fig. 20), joined by the tube *d*, and of a thick-walled glass tube *c*, of $\frac{1}{2}$ to 1 mm. internal diameter, and bent as shown in the figure.

This tube we will call the *capillary tube.* The

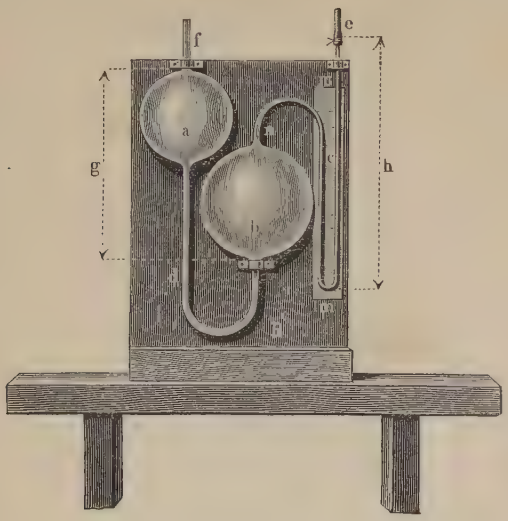

Fig. 20.

bulb *a* holds about 100 ccm., and *b* about 150 ccm., so that when 100 ccm. of gas is brought into *b*, sufficient space for the absorbing liquid will remain. To protect the pipette from being broken and to facilitate its manipulation, it is screwed to a wooden or iron standard.. On account of the different behaviour of wood and glass toward changes of temperature and atmospheric moisture, it is advisable to fasten the glass

at only three places by means of metal bands and sealing wax, the capillary tube being allowed to project from 2 to 3 cm. above the frame.

A short piece of rubber tubing is wired on to the free end of the capillary. The distance h must be greater than g, so that it may be possible to enclose a gas between two columns of liquid in the pipette. A white porcelain plate is set in at m to render the liquid in the capillary tube more distinctly visible.

B. The Simple Absorption Pipette for Solid and Liquid Reagents.

The only difference between this and the simple

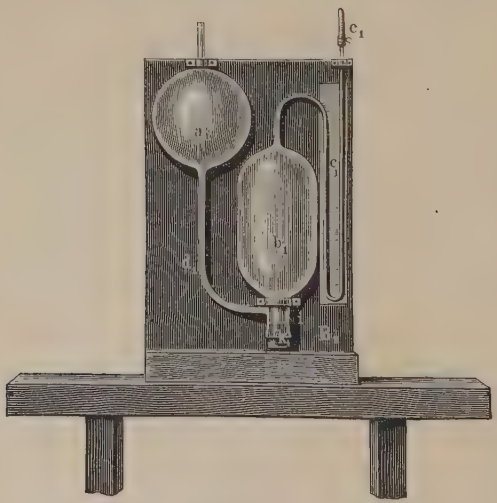

Fig. 21.

pipette is that in place of the bulb b there is inserted

the cylindrical part b_1 (Fig. 21), which can be filled with solid substances through the neck i and the opening l in the wooden base. A cork or rubber stopper, held in place by a wire, closes the neck i.

A glass tube closed at the top, and over which a rubber ring, cut from a rubber tube, is drawn, also makes a good stopper. By this arrangement only a narrow strip of rubber is exposed to the action of the reagent (Fig. 21*b*).

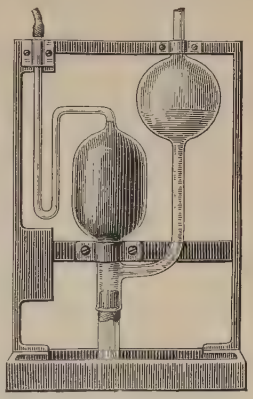

Fig. 21*b*.

Double Absorption Pipettes.

Reagents which are acted upon by oxygen, *i.e.* potassium pyrogallate, cuprous chloride, ferrous salts, etc., cannot of course be kept in the above form of pipette, since the reagent in a would become inactive in a short time through contact with the air. The author sought to avoid this difficulty by protecting the reagent with a layer of high-boiling petroleum, after first convincing himself that the tension of the petroleum, resulting from its solubility in the reagent, did not cause a perceptible error. It was soon found, however, that although such hydrocarbons lessen decidedly the access of air, they do not by any means form a perfect protection. Further experiment with this object in view led to the construction of—

C. The Double Absorption Pipette (Fig. 22).

This pipette permits the use of the reagents in question under an easily movable atmosphere which is free from oxygen, and the reagent employed may be kept completely saturated with those constituents of the gas that it does not strongly absorb, this being a

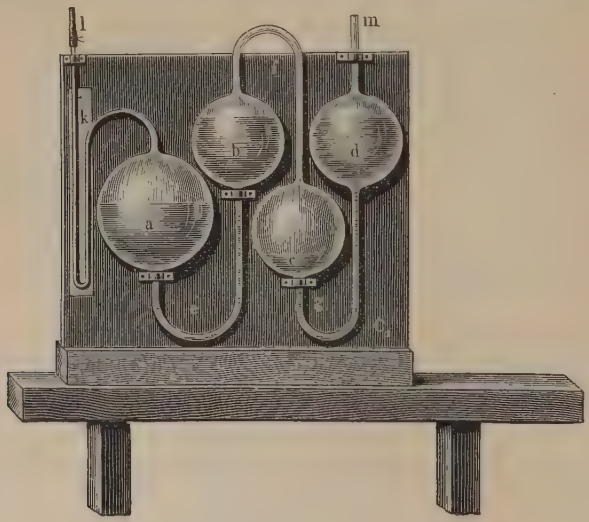

Fig. 22.

great advantage. The pipette consists of the large glass bulb *a*, of about 150 ccm. capacity, and three smaller bulbs, *b*, *c*, and *d*, each containing only 100 ccm. They are connected by the bent tubes *e*, *f*, and *g*, and end in the bent capillary tube *k*.

The pipette is fastened to a wooden standard in the manner already described (see p. 33).

D. The Double Absorption Pipette for Solid and Liquid Reagents (Fig. 23).

The construction may be easily understood from the figure and from what has already been said.

To prepare the double pipettes for use, introduce the solid substance to be employed, and then fill the

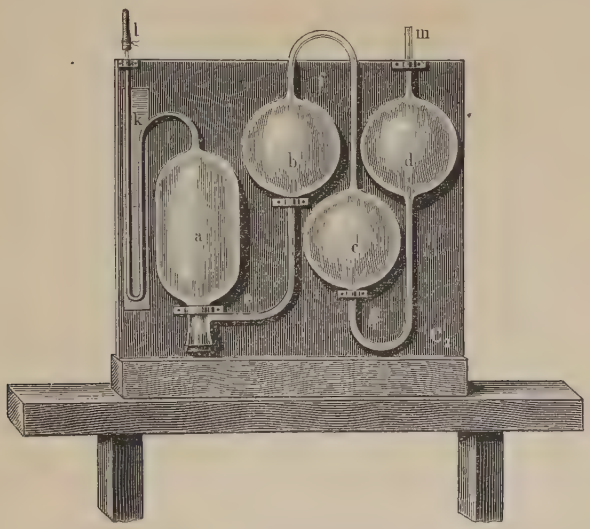

Fig. 23.

pipette completely with the gas to be analysed by slowly drawing the gas through. Now pour some water through *m* into the bulb *d* until *g* is full. Close the rubber tube *l* with a pinchcock, insert into it a thin glass tube at least one metre long, and fasten a

funnel to the upper end of the latter by means of a piece of rubber tubing.

Upon pouring the reagent into the funnel, the pressure given to it by the long tube enables it to quickly pass through the capillary tube *k* into the bulb or cylinder *a*. This can be still further hastened by gentle suction at *m*.

After about 100 ccm. of the reagent have been introduced, the bulb *d* is nearly filled with water, and the gas remaining in *a* is driven out through the long tube by blowing into *m*. The pipette is now closed at *l*, and shaken for some time to remove from the bulb *b* the gases absorbable by the reagent. After any gas bubbles which may now be in *a* have been driven out, suction is applied at *m*, and so much gas is sucked out of the bulb *b* that the liquid in *d* will enter and completely fill *c*. If the water first poured in is not sufficient, more must be added from time to time.

In pipettes thus prepared the tubes *k* and *e* and the bulb *a* are filled with the absorbent, the space from *b* to *f* with a gas free from oxygen, *c* and *g* with water, and *d* with air (Fig. 22). While the reagent in the simple pipette may be considered to be saturated with gas only when it is kept in continual use, that in the double pipette, on the contrary, remains saturated for an exceptionally long time, since the diffusion must take place through the confining 100 ccm. of water and through the narrow tube *g*. The error caused by this theoretical possibility may be wholly disregarded in using the pipette. When a new filling of the pipette is necessary, the reagent may easily be driven out by means of the rubber pump (Fig. 11), which is put on at *l*.

Manipulation of the Absorption Pipette.

To analyse a gas with the apparatus described, the burette is filled with distilled water, which has been previously saturated, by shaking, with the gas in question.

If simple pipettes are used, these are so filled with the absorbent that the bulb *a* remains empty. The absorbent also must be saturated, by shaking, with the gases which are but slightly soluble in it.

The saturating of liquids is best done in a flask half filled with the same, a rapid stream of gas being led through the liquid, and the flask vigorously shaken.

In technical work, where the same analyses are repeatedly made, the absorbent is kept saturated through continual use.

If the pipettes have the temperature of the room, as can easily be ascertained by introducing a thermometer at *k* (Fig. 24), the analysis is begun by drawing the gas into the measuring tube in the manner already described. It is convenient to take exactly 100 ccm. (see p. 24), so that the results may be read off directly in per cents.

The apparatus is now arranged as shown in the figure.

The pipette is placed on the wooden stand *G* and is connected with the burette by the capillary tube *F*, which is a piece of thermometer tubing of about 0·5 mm. internal diameter.

To avoid the enclosing of air bubbles, the rubber tube *d* is first filled with water by means of a capillary funnel, and the capillary *F* is then introduced. *F* is

thus completely filled with water. The rubber tube *i*

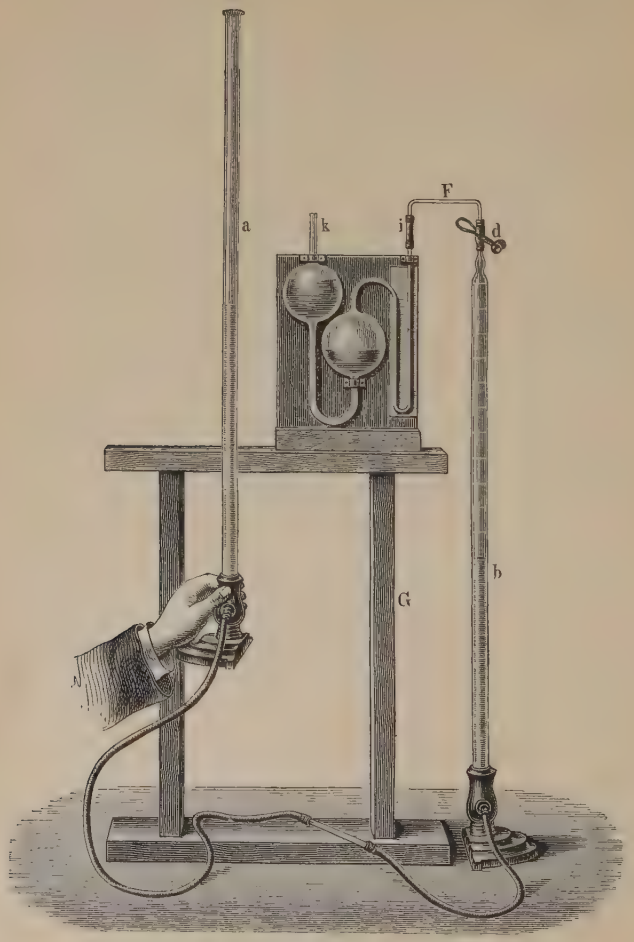

Fig. 24.

of the pipette is squeezed between the thumb and the

first finger of the right hand, and while thus compressed and free from air, the capillary connecting tube is inserted.

Upon raising the level-tube *a* and opening the pinchcock, the gas passes through the connecting tube into the absorption pipette. Any small air-bubbles which may have been enclosed when *F* was inserted into *i* are, at the beginning, separated from the gas by the water in *F*. If these bubbles do not take up more than 5 to 10 mm. space in the capillary of the pipette, they may be disregarded, since the error arising therefrom is about 0·03 ccm. If the bubbles are larger, although with a little cleverness this may always be avoided, the gas is brought back into the burette by lowering the level-tube, and the operation is repeated.

When the gas has passed over into the pipette, about $\frac{1}{2}$ ccm. of water is allowed to follow, this water serving to rinse the capillary and to free it sufficiently from the absorbing liquid which it previously contained. The gas is now enclosed between two columns of liquid, the absorbent on the one side and the water in the capillary on the other.

The burette having been closed by the pinchcock, the pipette is disconnected and shaken, and the absorption of the gas thus effected.

The burette and pipette are then reconnected, the level-tube is placed on the floor, and the gas is brought back into the burette, care being taken that the absorbing liquid does not pass farther than the connecting capillary *F*. The pinchcock is closed, the pipette removed, and the reading of the remaining volume is made as before described.

The manipulation of the pipettes filled with solid absorbents is still simpler, for in this case no shaking is necessary, because of the large surface of contact between the solid and the gas. On this account also the apparatus need not be disconnected.

A separate pipette is used for each absorbent, and aside from the economy of reagents, the frequent cleaning of the apparatus is thus avoided. An especial advantage is, further, the complete assurance that no loss can take place through ill-fitting glass or rubber stopcocks while the gas is in the pipette or when the pipette is vigorously shaken, and that without fear of error due to the taking up of gases not chemically absorbable, large amounts of reagent may be used, and the work be thereby greatly shortened. After using, the pipettes are closed at *i* with a piece of glass rod, and at *k* with a small cork, and upon a piece of paper fastened to the back of the standard by thumb-tacks is written the number of cubic centimetres of gas which the reagent has absorbed.

If the absorbing power of the reagent is known (see p. 111), waste may be avoided, and with one filling of the pipette several hundred analyses (the number depending upon the nature of the gases examined) may be made, with certainty throughout as to the efficiency of the absorbent.

If the work has not been carelessly done, the gas burette stands ready for the next analysis. If on the other hand reagents have been allowed to enter the burette, it must be cleaned, its simple construction rendering this quite easy.

Some gases are completely absorbed by leading them over into the pipette, while others must remain

in the pipette for a certain length of time. By using a small sand-glass, the operator is enabled to give his whole attention to the analysis proper, without fear of allowing too little or too much time to elapse.

CHAPTER III

APPARATUS FOR EXACT GAS ANALYSIS

General Remarks

The extremely simple and exact gasometric methods proposed by Bunsen do not admit of the rapid performance of a large number of exact analyses, because the absorption of the gases takes too much time. Doyère,[1] Frankland[2] and Ward, Regnault,[3] Reiset,[3] Russel,[4] Parry and others have constructed various forms of apparatus which render rapid work possible through the use of liquid reagents and of mechanical appliances which in some cases are very complicated.

The method devised by Doyère is superior to that of Bunsen, in that the analysis is carried out in glass vessels fused together, and all ground joints and rubber connections are avoided: it has, however, the fault that great accuracy can be obtained only by the use of very cumbersome apparatus.

By the introduction of a different manner of measuring and a somewhat changed construction of

[1] *Ann. Chim. Phys.* [3] **28**, p. 1.
[2] *Jour. of the Chem. Soc.* 1868, p. 109.
[3] *Ann. Chim. Phys.* [3] **26**, p. 333.
[4] *Jour. of the Chem. Soc.* April 1868.

the necessary absorption pipettes, the author has endeavoured to improve the Doyère method, so that, in its changed form, rapid and very exact work may be possible without the use of delicate physical instruments.

Bunsen measures the gases under varying pressure and varying volume, and Doyère measures them under constant pressure and varying volume, while in the method about to be described the measurements are made under constant volume and varying pressure. Following Mariotte's law, the values so found bear the same proportion to one another as do gas volumes under the same pressure.

If the gases are saturated with moisture when measured, corrections for the tension of aqueous vapour and for barometric pressure are unnecessary.

Doyère[1] measures the gases in a Bunsen eudiometer, and he avoids correction for pressure by joining the eudiometer with an iron holder having a screw attachment, by means of which the mercury in the tube and in the suitably formed trough may be brought to the same level. The readings are made with a special telescope of great exactness. The absorptions are made in Doyère's improved Ettling gas pipette.

The manipulation of the pipettes demands that the eudiometer at some place in the mercury trough may be brought wholly beneath the level of the mercury, and further, that the suction tubes of the pipettes be as long as the eudiometer. From these two particulars it results that when a very deep trough is used, the pipettes are very unwieldy and easily broken, or that

[1] *Ann. Chim. Phys.* [3] **28**, p. 1. Fehling's *Handwörterbuch der Chemie*, vol. i. p. 512.

when a shorter eudiometer is employed, a sharp reading of the scale can be made only with the most perfect instruments, since it must be possible to measure with exactness tenths of a millimetre.

Doyère states that the measuring tubes used by him have a length of 20 cm. and an internal diameter of 15 mm. For large gas volumes he uses vessels similar to those employed by Bunsen for this purpose, the lower part being cylindrical and graduated, and ending above in a bulb.

The method here to be described permits, by the employment of spherical measuring vessels, the use of a shallow mercury trough and of shorter, more easily manipulated, and less fragile gas pipettes, and a measurement more than three times as sharp, since with this apparatus, if the gas at the beginning of the analysis nearly fills the bulb at atmospheric pressure, the scale has an available length of 760 mm. while Doyère's measuring tube is only 200 mm. long.

The measurements are made under constant temperature and constant volume but varying pressure. This is accomplished by expanding the gases to a certain volume in small glass bulbs, which can easily be brought into communication with a barometer. The expanding is done by lowering a movable vessel filled with mercury. The pressure exerted by the gas is then read off on the barometer scale. The absorptions are made in the gas pipettes to be described later.

Description of the Apparatus.

Fig. 25 gives a sectional view of the apparatus. The iron mercury trough A is fastened to the wooden

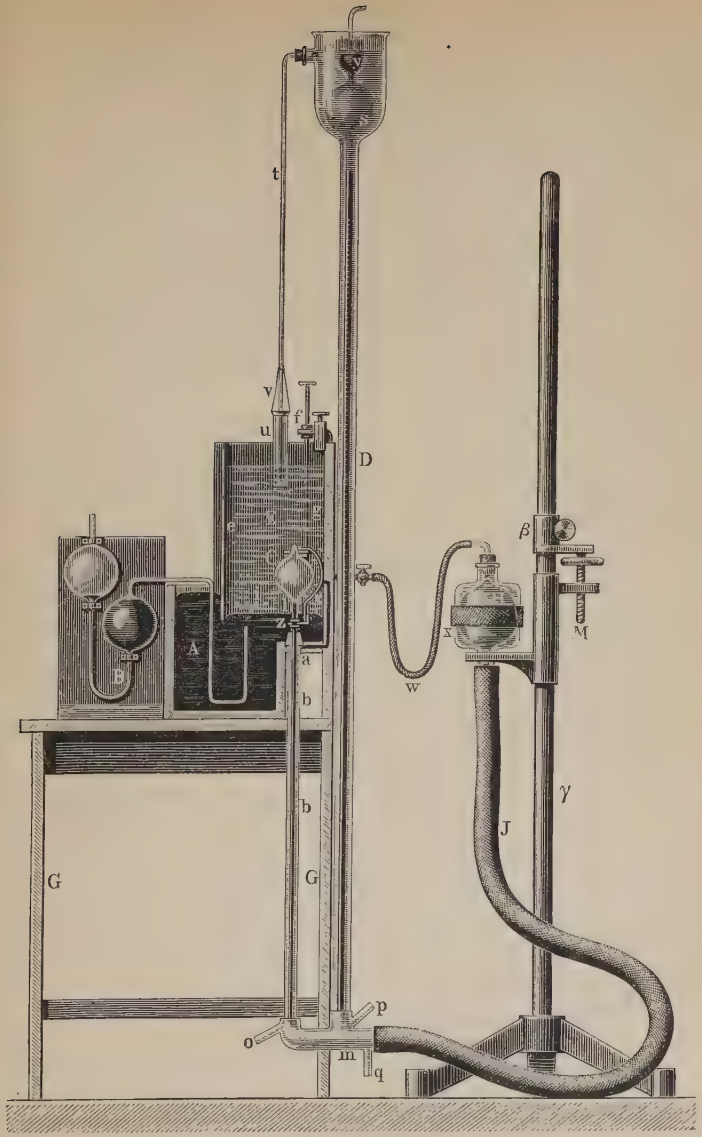

Fig. 25.

stand *G*, and is connected with the graduated barometer tube *D* by the iron tube *b*. The barometer tube is connected at *m* by means of a rubber tube *J* with the level-bulb *H*. The upper part of the mercury trough consists of the reservoir *E*, whose overflow tube (this is not given in the drawing) can be connected with a barrel by means of glass or rubber tubes.

The sides of the water reservoir *E* are glass panes, one of which *e* extends only so deep into the mercury as to leave it easily possible to bring under it the end of the capillary tube of the pipette *B*. The measuring bulb *C* serves to hold the gas. The tubes *b* and *D* are surrounded with larger glass tubes, and the rubber tube *J* is double, so that *b*, *D*, and *J* may be cooled with water. By means of a glass tube with three arms (this tube does not appear in the figure) water is admitted simultaneously through the tubes *o*, *p*, and *q* when the apparatus is in use. *o*, *p*, and *q* are joined to the three-arm tube by rubber tubes supplied with glass stopcocks. A part of the water enters at *o*, surrounds *b*, and enters the water reservoir *E* through a small canal *r*. The water entering at *p* surrounds the barometer tube *D* and its bulb *s*, and runs through a side opening and the tube *t* into *E*. To prevent the spattering caused by the air bubbles drawn along with the water, a wider tube *u* is hung upon *t* by means of the thread *v*. A third stream of water entering at *q* passes through the outer rubber tube of *J*, and through the double-walled level-bulb and the rubber tube *w*, into *E*.

The outer wall of the level-bulb is simply made by joining together the ends of two broken bottles by the rubber band *x*. The rubber tube *w* is joined

to the bulb by means of a cork and a bent glass tube.

By this arrangement it is possible to keep all parts of the apparatus at the same temperature.

The author earlier obtained a constant temperature by connecting the apparatus directly with the water supply pipes. A great drawback here, however, is that in summer, when the temperatures of the air and the earth are markedly different, it takes considerable time for the temperature to become constant, and further, the apparatus becomes heavily covered with moisture when it is cooled at times below the dew-point of the air. The author now prefers to place the apparatus in a room with north exposure. In this room are two barrels of the size of ordinary petroleum barrels. One of these stands at an elevation, the other on the floor. By means of a small iron suction-pump, such as is everywhere for sale, the water may be raised from the lower to the upper cask. During the analysis the water is allowed to run through connecting glass tubes and through the apparatus into the lower barrel, and at the end of the work it is pumped up again. Provided that the temperature of the room undergoes no great changes, it is easily possible by this simple means to keep the variations of temperature in the apparatus under 0·2°. Since the water and the apparatus at the beginning of the research have approximately the same temperature, the temperature becomes constant in a very short time.

The barometer tube *D* of the apparatus ends in the bulb *s* and the cup *y*, the latter being closed by a stopper.

The barometer vacuum is produced by closing the

tube *b* at *z* with a piece of rubber tubing, and then, having opened *y*, driving the air out of the bulb *s* by raising the level-bulb. The air adheres tenaciously to the walls of the apparatus, but by repeating this operation several times, it is possible to remove the air almost completely.

Finally, while the bulb *s* is almost wholly filled with mercury, a few drops of water are introduced through *y* into *s*, the stopper is tightly inserted and some mercury is poured into the cup: not a trace of air can then enter the barometer tube through *y*, because the opening is completely closed with mercury.

The Measuring Bulb.

The measuring bulb *E* (Fig. 26) is fastened to the iron holder *g* by means of the projecting tubes *r* and *s*; *r*, which is closed at the top, is about 5 mm. long and *s* about 30 mm. At from 5 to 7 mm. below the bulb, *s* is widened into a collar *x*, by softening the glass tube in the blast-lamp flame, and pressing it together. The iron holder *g* has at *t* a thick perforated sheet-iron cap for holding *r*. The holder bends around the bulb and is supplied at the lower end with the perforated iron plate *u*, which is bent at a right angle, and holds the projection *s*. *u* may be set where desired by means of the screw *v*, to which the slot through which it passes gives a play of several millimetres. *s* projects 4 to 5 mm. beyond the plate *u*. The iron collar *y* is fastened to *g* in such a position that it just slips under the fork *f* when the holder and bulb are placed over the end of the iron tube passing

through the rubber stopper *m*, and are firmly pressed against the rubber. The fork is firmly fastened to the slide *i*, which can be moved up and down by the screw *h*. By screwing the slide down, the measuring bulb can be pressed against the rubber stopper and a tight connection with the barometer tube thus be obtained. A scale upon the slide *i* and its guides makes it possible to bring the bulb at different times into exactly the same position as regards the millimetre scale of the barometer.

The total height of the measuring bulbs varies from 7·5 to 9·5 cm.

Since the walls of the measuring bulbs used by the author are only as thick as those of ordinary bulb pipettes, it was thought possible that, in the measurement of very small gas volumes, the

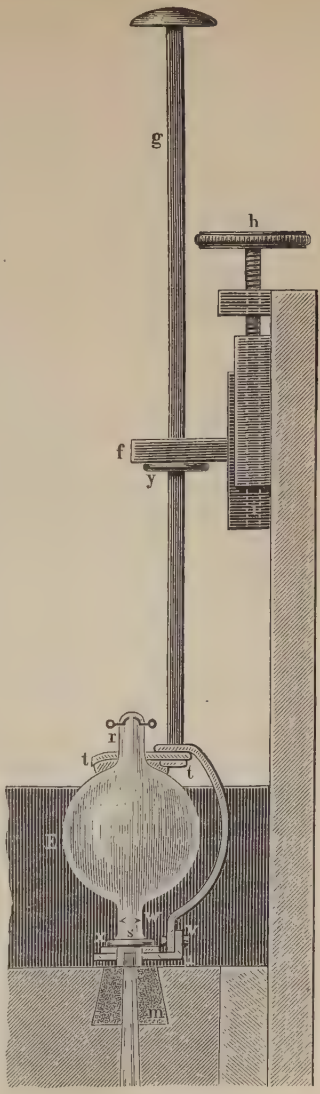

Fig. 26.

volume of the bulb might be decidedly changed, since under such conditions it is exposed to nearly the full pressure of the atmosphere.

To settle this question, the volume of the bulb, first empty and then filled with gas, was determined in a stereometer, and it was found that even with large bulbs of 100 ccm. capacity no measurable difference of volume could be detected; hence even thin-walled glass bulbs may be used without hesitation for these measurements.

The Sliding Level (Fig. 27).

This consists of the glass bulb *a*, of from 150 to 200 ccm. capacity, and terminating in the two tubes *h* and *i*, which are about 7 cm. long and 1 cm. wide. The bulb is supported by the clamp arrangement β and the stand γ (Fig. 25).

This clamp arrangement, of which front and side views are given in Fig. 27, is made up of the tube *a* (which slides easily upon the rod of the stand, and which can be made fast by means of the open ring *c* and the screw *b*), the micrometer screw *d*, the guide *e*, and the support *f* which carries the bulb. The lower glass tube of the bulb *a* is connected with the mercury trough by the rubber tube *G*.

f_2 is fork-shaped, the two arms being wide enough apart to allow the glass tube to pass easily between them. The upper support f_1 is perforated to admit the tube *h*. Hence the bulb may be detached from the holder by raising the bulb somewhat, slipping *i* out of the fork f_2 and drawing *h* out of f_1.

Upon loosening the screw *b*, the level can be easily moved up and down, and it can be fastened in any

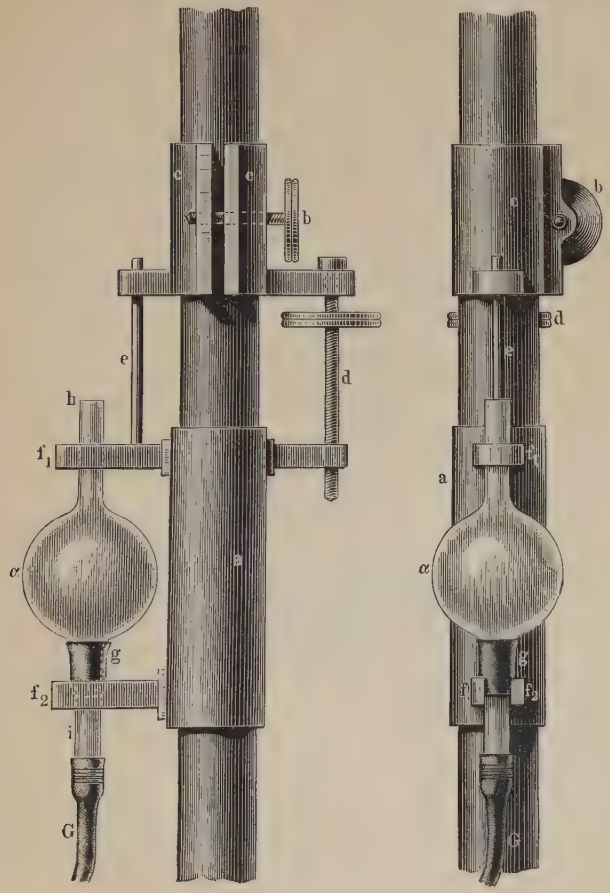

Fig. 27.

desired position by screwing *b* tight and adjusting with the micrometer screw *d*.

The Gas Pipettes.

The gas pipettes were devised by Ettling and were first used by Doyère as absorption vessels for gas analysis.

They consist of two bulbs *a* and *b* (Fig. 28), of the same size, joined together by the tube *c* and ending in

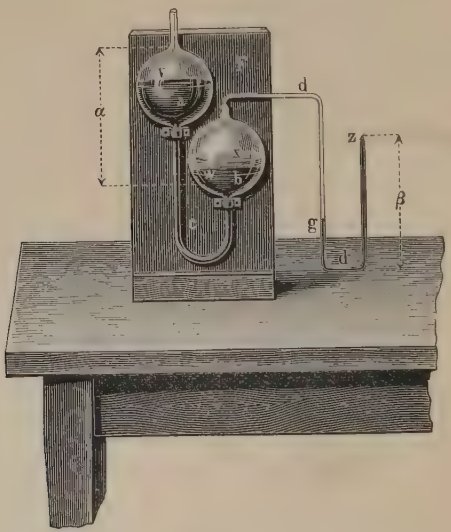

Fig. 28.

the bent capillary tube *d*. A very small bore thermometer tube, and not a tube of 1 mm. bore as Doyère suggests, is used as the capillary, thus making it easy to avoid the introduction of absorbent into the measuring bulb or the remaining of any considerable quantity of gas in the pipette.

Gases move rapidly in capillary tubes, but liquids, especially concentrated solutions of salts, move very slowly; hence it is easily possible to bring the gas residue in the pipette to less than $\frac{1}{1000}$ of a cubic centimetre without danger of the absorbent entering the measuring bulb. It is almost impossible to do this when wider glass tubes are used.

The pipettes must be so made that the distance a (Fig. 28) is only as large as or smaller than β: the capillary must be bent close to the bulb b. The pipettes are fastened to the wooden standard in such a manner that the capillary d comes to within a few millimetres of the bottom of the mercury trough when the pipette is placed in the position shown in Fig. 25.

The bulbs of the pipettes must be considerably larger than the volume of the gas to be brought into them. The inconvenience of carefully cleaning the pipette after the absorption is avoided by using a special pipette for each reagent. Pipettes of very different sizes are employed, the sizes depending naturally upon the dimension of the measuring bulbs.

To bring a measured amount of the absorbent into the pipette, which is first filled with mercury, connect it by means of a piece of rubber tubing e (Fig. 29) with the small burette f containing the reagent and supported by the clamp g. Open the pinchcock h, slip a rubber tube over the burette at i, and by suction so exhaust the air in the burette that any gas remaining in the pipette will be drawn through the capillary x and through the absorbent. The pipette is thus completely filled with mercury. Stop

the suction as soon as the mercury is visible above the rubber *c*, put the rubber tube on the pipette at *l*,

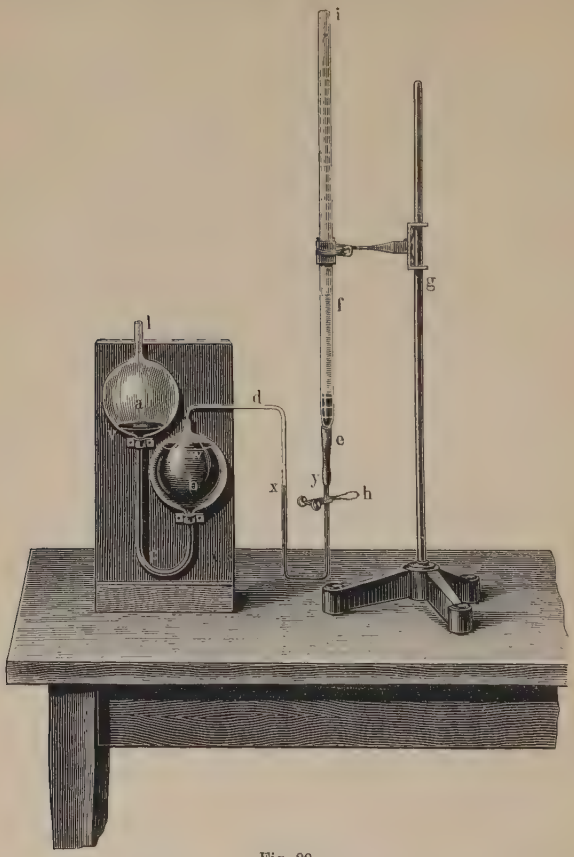

Fig. 29.

and draw the mercury back to the capillary. Note the height of the absorbent in the burette, and then suck the desired amount of the same through the

capillary *d* into the pipette. At the moment when the necessary amount of reagent has passed over, bring a drop of mercury into the burette at *i*.

The amount of the absorbent introduced may be sharply determined by drawing the mercury into the pipette until the reagent is again visible in the capillary *d*, and then noting the height of the reagent in the burette.

The pipette thus prepared for the analysis contains mercury between *v* and *w*, between *w* and *x* the absorbent, and from *x* to *y* mercury; to remove any reagent adhering to the outside, the capillary is dipped into a beaker containing distilled water and is then carefully dried with filter paper.

Gas Pipettes for Solid Absorbents.

To bring the gases under examination into contact with solid absorbents, the form of pipette shown in Fig. 30 is used. In this the tube *c* has a branch tube *e* through which solid substances, such as sticks of phosphorus, are introduced into the bulb *b*; *e* is then closed at *f* with a cork and the pipette is

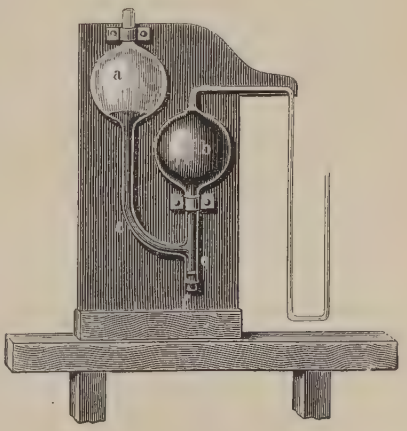

Fig. 30.

filled as usual with mercury. When a gas is drawn in, the solid substances remain in the bulb *b*, and so come into contact with the gas.

The Explosion Pipette.

Combustions are made in an explosion pipette (Fig. 31). This has at *f* two platinum wires and at *g* a glass stopcock. The wires are fastened to two screw-eyes, to which are connected the wires from the induction apparatus. To explode a gas mixture, it is brought into the pipette, the stopcock is closed, and into the end of the capillary at *z* a fine sewing needle is inserted, which prevents the mercury being thrown out of the capillary by the strong pressure during the explosion.

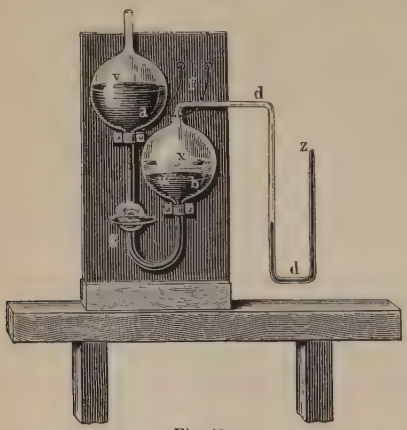

Fig. 31.

The Measurement.

For making the measurement, the bulb *C* (Fig. 25) is firmly pressed down upon the rubber stopper at *a*, and the level-bulb is lowered until the meniscus of the mercury column at *l* exactly coincides with the cross-hair of a magnifying glass fastened to the

mercury trough. (This magnifier does not appear in the figure.) The reading of the barometer tube, which is best done by means of a telescope, gives then directly the pressure of the gas; this pressure is obviously independent of barometric changes, since the barometer vacuum is closed with mercury. If the gas being measured is saturated with moisture, the correction for the tension of aqueous vapour is unnecessary, because there is in the bulb of the barometer aqueous vapour which at the same temperature exercises the same pressure in an opposite direction.

The exact adjustment is made with the micrometer screw of the level-bulb, and the reading on the scale is then immediately made with the telescope. It is advisable to repeat both the adjustment and the reading.

The temperature, as shown by a thermometer placed near the measuring bulb, is also noted.

If the temperature has not changed during the work, and if the mark on the measuring bulb corresponds with the zero mark of the barometer scale, the values so found may, with allowance for the correction of the apparatus (see below), be directly calculated to per cents. If, however, changes of temperature have taken place, the necessary corrections therefor must be made.

It is here presupposed that the zero mark of the barometer scale lies in exactly the same horizontal plane as the cross-hair of the magnifying glass. Long experience has convinced the author that it is simpler to bring the cross-hair only approximately into the plane of the zero mark, and at the same

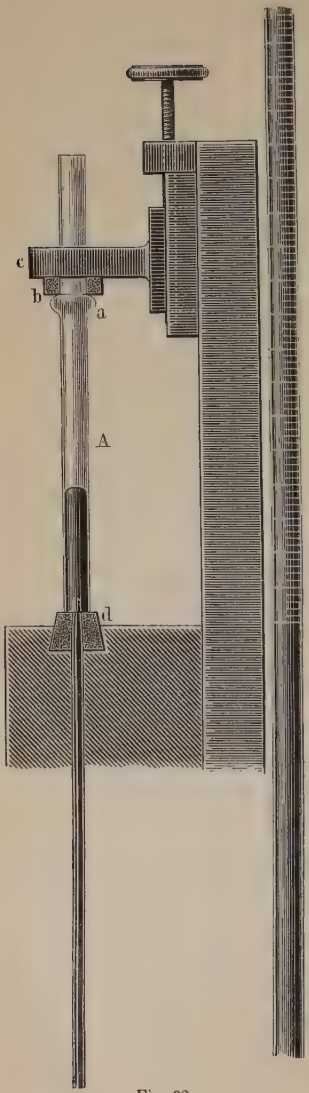

Fig. 32.

time to forego complete vacuum, and after putting the apparatus together, to determine the correction for both errors by comparison with a barometer. This is best done with the aid of a simple glass tube *A* (Fig. 32), supplied with the cork *b*, and widened at *a* by heating it and pressing it together, the tube being firmly pressed against the rubber stopper *d* by means of the holder *c*. When the meniscus of the mercury in the tube coincides with the cross-hair of the magnifier—this being effected by moving the level-bulb —the reading of the barometer tube must give the barometric height less the tension of aqueous vapour. The difference between this result and that given by a good barometer is the *correction of the apparatus*. Provided that the apparatus is not moved this correction never changes.

A measuring bulb of such a size is chosen that in the beginning of the analysis the gas to be examined completely fills it. In all analyses in which the greatest accuracy is not aimed at, the readings need be exact only to 0·25 mm. A variation of 0·1 degree in the determination of the temperature of the gas corresponds to an error of 0·04 per cent, and without special arrangements it is impossible to avoid this. On the other hand, with a pressure of 760 mm. at the beginning, an incorrect reading of 0·3 mm. causes the same error, so that it is useless to try to obtain greater accuracy in the readings by the use of a very finely divided scale.

Taking it for granted that the calibration is correct, errors in measurement due to incorrect readings can take place only in very careless work. The size of the errors which are caused in ordinary work by changes of temperature, incomplete saturation of the gases to be measured in a moist condition, solubility in the absorbent, etc., is shown in the analyses given later.

The Absorption.

The gas pipettes already described are used for the absorptions, the manipulation being shown in Fig. 33 and Fig. 34.

Fig. 33 gives the position in which it is possible to bring the gas completely into the pipette. The measuring bulb is here brought below the surface of the mercury and the gas is drawn into the pipette by sucking with the mouth on a rubber tube attached to *m*. The suction is discontinued at the moment

when the mercury begins to flow from the capillary into the bulb of the pipette.

The pipette then contains (see Fig. 28) mercury

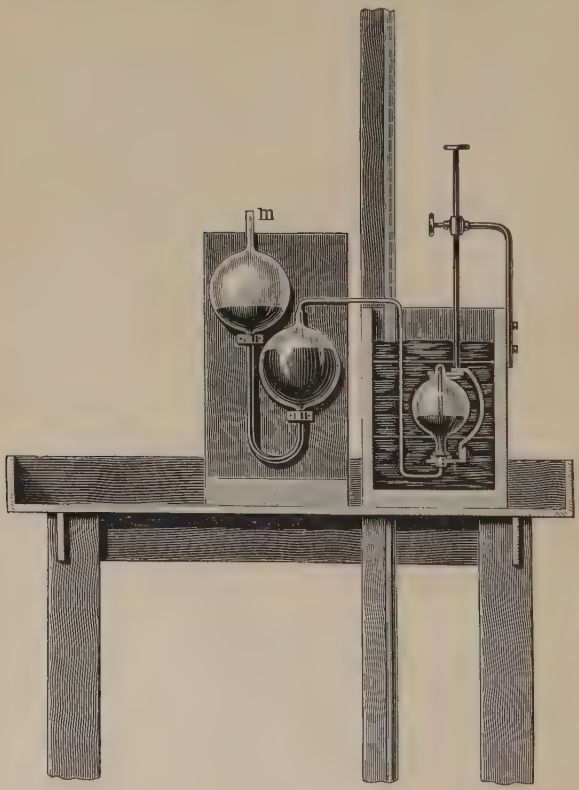

Fig. 33.

from v to w, absorbent from w to x, gas from x to g, and mercury from g to z, so that the pipette, after it is taken out of the mercury trough, may be vigorously shaken and a rapid absorption effected.

To drive the gas from the pipette back again into

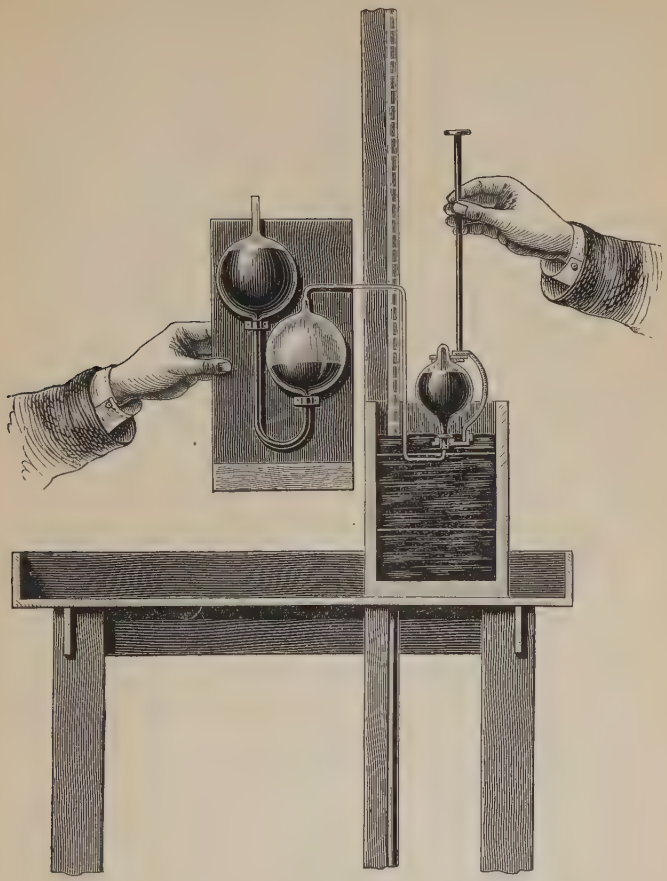

Fig. 34.

the measuring bulb, the apparatus is brought into the position shown in Fig. 34.

One must at first blow into the pipette at *m* to

set the gas in motion; when it has once started, the mercury in the measuring bulb acts with an aspirating effect, so that the gas passes over of itself. At the moment when the absorbent has risen to about 1 cm. from the end of the capillary in the measuring bulb, the capillary is lowered under the mercury and mercury is drawn into the capillary by sucking on the rubber tube attached to *m*. In this manner the entering of reagent into the measuring bulb may be avoided with certainty.

If a gas thread about 1 cm. long remains in the capillary, this corresponds to approximately 0·001 ccm. of gas, since the total 35 cm. length of the capillary has a volume, determined by weighing the mercury which it holds, of 0·038 ccm. Hence from this source no appreciable error arises.

The analysis is made as follows:—

Fill the carefully cleaned and moistened measuring bulb with the gas under examination by lowering the bulb into the mercury in the trough, drawing out the air in it with a gas pipette, and bringing the gas into the bulb either by means of a delivery tube brought under the mouth of the bulb, or by means of a gas pipette.

The necessary measurements, absorptions, and explosions now follow, their order being determined by the nature of the gas.

Since difficulties arise only in the use of fuming sulphuric acid over mercury, while all other reagents can be easily manipulated in the manner already described, the reader is referred to the second part of the book for descriptions of the absorptions of the various gases.

The heavy hydrocarbons cannot be absorbed with fuming sulphuric acid in the manner described, because, on bringing together the fuming acid and mercury, sulphur dioxide is evolved even in the cold, and acid sulphates are formed which, upon long standing, separate as thick crusts and obstruct the pipette. Since, however, the gases which are not absorbable by the fuming acid are very insoluble in the same, a pipette completely filled with the acid may be used, the mercury here coming into contact with the sulphuric acid only in the capillary tube. If care be taken in the manipulation that no mercury passes over from the trough into the pipette, and if, after using, all mercury be removed from the capillary by means of a common suction pipette attached thereto, so that sulphuric acid alone remains in the pipette, a stoppage of the capillary, which, when it has once taken place, is difficult of removal, need not be feared.

To protect the lungs from the fumes of the sulphuric acid, a glass tube filled with pieces of caustic potash is interposed between the rubber suction tube and the pipette.

The gases being examined do not here, as in the other absorptions, come in contact with but small amounts of the reagent, hence the errors which might result from the solubility of the gases that are not in an analytical sense absorbable, could not be disregarded. To obtain an idea of the solubility of the gases in question, illuminating gas was freed from the heavy [1] hydrocarbons and carbon dioxide by absorption, and the residue,

[1] By "heavy" hydrocarbons are meant those which are absorbable by fuming sulphuric acid.

consisting of oxygen, carbon monoxide, hydrogen, marsh-gas, and nitrogen, was brought in contact with a large quantity of fresh sulphuric acid.

The volume of the residue was determined before and after, and it was found that the change in volume could not be measured. Hence the solubility of the gases not absorbable by sulphuric acid may be wholly disregarded.

The data of the experiment were the following:—

About 25 ccm. of illuminating gas was allowed to stand for some time in contact with sulphuric acid, was then freed from sulphur dioxide and the fumes of sulphuric acid by caustic potash, and was measured moist. The result was 757·7 mm. pressure at 16·8° C. The gas was then shaken in a pipette with fresh concentrated sulphuric acid, and after standing for two hours it was brought into the measuring bulb and measured moist. Result—757·7 mm. at 16·6° C.

The Mercury Trough without Barometer Tube.

Fig. 35 shows the arrangement of the apparatus in its simplest form, a form which the author considers especially practical. The apparatus consists of an iron mercury trough *A* (on account of the presence of water, wood cannot be used, since it would swell and change form), of a glass tube *D* graduated in millimetres and from 76 to 80 cm. long, and further, of the wooden stand *G* and the water reservoir *E*. The sides of the water reservoir *E* are glass panes, one of which *e* extends only so deep into the mercury as to leave room to bring the capillary of the pipette *B* under it into the measuring bulb *C*.

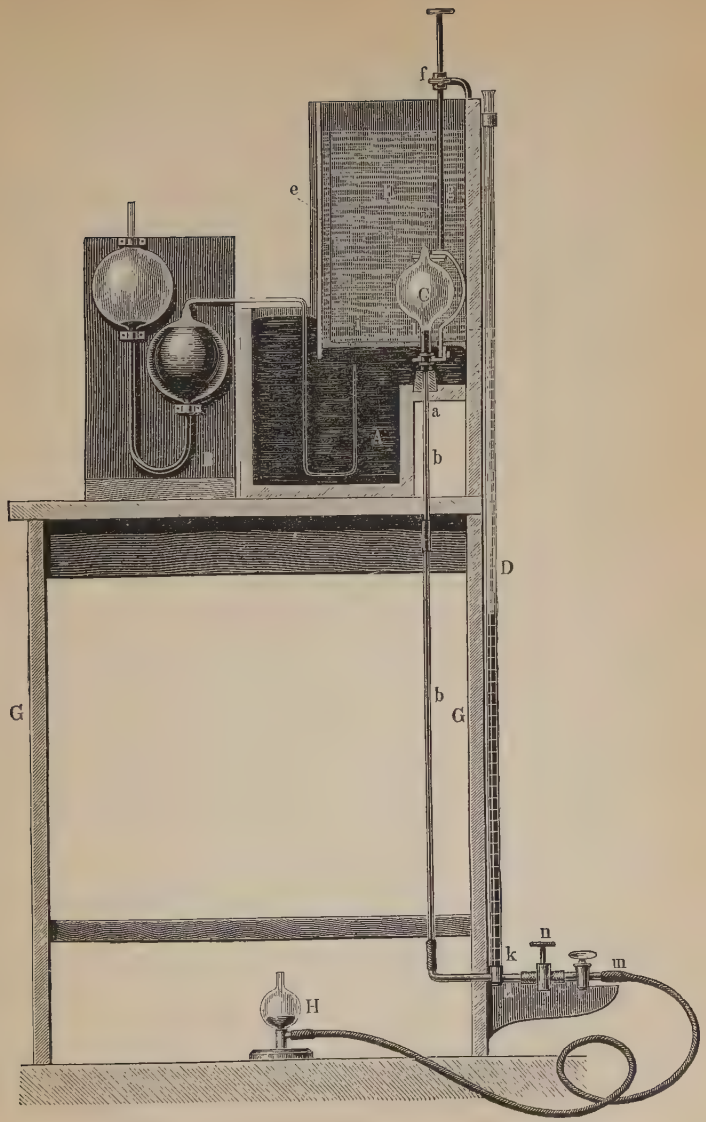

Fig. 35.

By placing the measuring bulb upon the rubber stopper *a* in the mercury trough, it can always be brought, by means of the holder *f*, into mercury-tight connection with the graduated tube *D*. The tube *b* and the ⊥-piece *d* are made of iron. *D* is connected with an arm of *d* by means of a piece of rubber tubing, which is wrapped in cloth to enable it to resist the pressure of the mercury. A cloth-covered rubber tube joins the other arm to the movable level-bulb *H*. For accurate adjustment of the mercury before taking the reading, the glass stop-cock *m* and the wide screw-clamp *n* are used, this device corresponding to that first employed by Pettersson.

For making the measurement, the bulb *C* is held firmly pressed against the rubber stopper *a* by means of the binding-screw *f*, and mercury is then let out through the cock *m* until the meniscus of the mercury in the measuring bulb exactly coincides with the line *i*.

In order to be always able to bring the measuring bulb *C* into the same position as regards the zero mark of the tube *D*, either the bulb has a little scale at *l*, upon which its position as regards the line *i* may be read, or there is on the rod *g* of the holder a mark at *f*, which during the measurement can be made to exactly coincide with the smoothly ground upper surface of the guide.

The readings are made with the naked eye, without use of the telescope.

Designating the barometric pressure by *b*, the pressure read on the scale by *d*, the tension of aqueous vapour corresponding to the temperature of

the water reservoir E by t, and the pressure of the gas in the measuring bulb by x, then

$$x = b - t - d.$$

If the apparatus is to be used only for those analyses in which the decrease in volume is but a small part of the initial volume, or, in other words, in which the pressure after the absorption is but slightly changed (*e.g.* in the determination of oxygen in the atmosphere), the tube D may then be made correspondingly shorter and the handiness of the apparatus greatly increased.

The manipulation may be understood from the descriptions given in the preceding pages.

CHAPTER IV

ARRANGEMENT AND FITTINGS OF THE LABORATORY

The room for gas analysis should have a north exposure, and should be supplied, if possible, with double doors and double windows. In building a laboratory the walls should be made exceptionally thick, and the ceiling and floor be of non-conducting material.

When the greatest accuracy is not required, a small water reservoir of the size of an ordinary petroleum barrel is large enough for furnishing the water for cooling the apparatus for exact gas analysis. This apparatus is placed in front of the window. After passing through the apparatus, the water runs into a small barrel from which it can be drawn up from time to time into the reservoir by means of a hand-pump.

In his researches upon the oxygen contents of the atmosphere, the author used a wooden reservoir of 2500 litres capacity, and obtained thereby a perfectly constant temperature throughout the work.

In winter the room is heated with gas when the temperature goes below 15° C. Ordinary gas stoves

cannot be used for this purpose, because they throw the heat too much toward the top of the room, thus causing too great differences of temperature in the various layers of air. The room can be heated in an entirely satisfactory manner by means of a thin-walled iron tube of about 7 cm. diameter. Beginning at the coldest point of the laboratory, the tube passes along the floor through the middle of the room, then up the farther wall, and near the ceiling it is carried out into the adjoining corridor.

For heating a well isolated room of 60 cbm. capacity, two ordinary Bunsen burners, inserted into the end of the tube, are sufficient even in the coldest days of winter. Since the tube gives up nearly all its heat, a small flame must be introduced into the perpendicular part of the tube through a little hole, to create the necessary draught. It is advisable to have the heating-tube of iron only so far as it is as warm as the hand, and to make all other parts of pasteboard. The reason for this is that all illuminating gas contains sulphur, and the products of the combustion, when cool, strongly attack the iron. A heating tube of this kind, made from pasteboard and iron, has done excellent service for a number of years.

The floor of the room must be mercury-tight. Board floors may be made tight by covering them with oil-cloth.

It is also convenient to have the floor slant from the sides towards a slight hollow, about 3 mm. deep, in the middle of the room. The mercury will then collect in the hollow, and can be easily taken up.

The room should further be provided with water-supply and sink. It is best to have the sink of

porcelain or stone, and to have it fitted with an arrangement for collecting the mercury inadvertently poured into it.

A barometer and an induction apparatus with battery are also necessary. Plates of thick glass resting upon simple iron supports fastened into the wall make a convenient shelf for holding the pipettes.

It is of great importance that the room be well lighted, and for this reason the gas laboratory should face a large open space if possible. A dark room may also be made much lighter by painting the walls white.

CHAPTER V

PURIFICATION OF MERCURY BY DISTILLATION IN VACUUM

Of all the methods used for purifying mercury, Weinhold's [1] distillation in vacuum is the most convenient. Unfortunately this does not yield a perfectly pure metal. The author has often found that other metals also distil over in vacuum.

A convenient apparatus for the distillation is that shown in Fig. 36. This corresponds in the main to Weinhold's device, but has some modifications. *A* is a bulb-tube, ground obliquely at the end, and extending to the bottom of the wide tube *D*. Through a stopper in the lower end of *D* is inserted from below a thin glass tube about 1 m. 6 cm. long, which reaches nearly to the bottom of the bulb *A*. The tube *C* is bent as shown in the figure, and has at *a* a side tube with glass stopcock. *D* is connected by a branch tube *b* and a piece of rubber tubing with the level-vessel *J*.

To start the apparatus working, the end of the tube *C* is closed at *c* by a piece of rubber tube and a

[1] Carl's *Rep. f. Exp.-Physik*, **15**, 1. Also *Fresenius Zeitschrift f. analyt. Chemie*, **18**, 252.

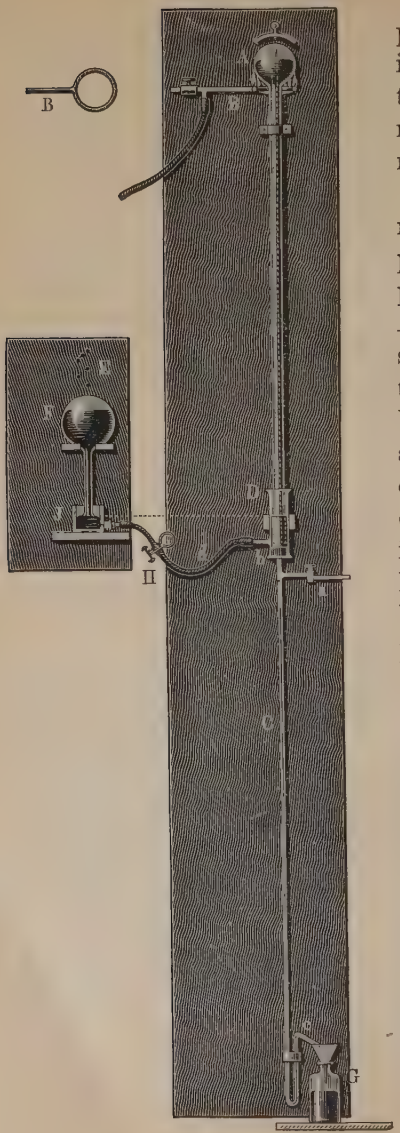

Fig. 36.

pinchcock, mercury is poured into *J*, and the apparatus is connected at *a* with a mercury air-pump.

As the air is removed from the apparatus, the mercury passes from *J* toward *D* and rises in the space between the tubes *A* and *C*. When the mercury air-pump yields only quite small bubbles of air, the exhausting is discontinued. The level-vessel *J* is now brought into such a position that the mercury, under the prevailing pressure of the atmosphere, fills about $\frac{2}{3}$ of the bulb *A*. To facilitate this adjustment the board *E*, which hangs upon a nail fastened into the wall, has a number of holes bored through it. By inserting the nail through one or another of these

holes, the position of the board may be easily changed. If now the bulb is heated by a ring burner, the mercury soon begins to boil, the vapours given off in the vacuum enter the tube *C*, condense there, and after a while the length of the column of mercury which has collected in the tube becomes greater than the height of the barometer. A bottle for receiving the purified mercury is then placed under *C*, and the rubber tube and pinchcock closing *c* are removed. It is advisable to stop the distillation, and after the apparatus has cooled somewhat, to exhaust the apparatus as completely as possible with the mercury air-pump. In this second exhaustion a considerable quantity of air which has been detached from the walls by the heat is always obtained. The apparatus must not be exhausted during the heating, because the mercury may break the whole apparatus by violently boiling when the pressure is decreased.

The ring burner *B* is made from a bent iron tube pierced with little holes, a circle of small, slightly luminous flames being thus obtained. A small screen of asbestos is hung above the bulb to check the upward radiation of heat.

With careful use the apparatus thus arranged may be employed for years, provided that the mercury introduced is always perfectly dry. To effect this the impure mercury is heated in an iron dish to 120°-130° C. The temperature may be easily ascertained by using a thermometer as a stirring rod. The mercury thus dried is poured when cool into the flask *F*, and this is closed with the thumb and inverted in the level-vessel *J*. During this manipulation the connecting rubber tube *d* is closed with the pinchcock *H*.

To distil, the pinchcock *H* is opened, and the apparatus may be left to itself for twelve hours, the height of the mercury in *A* being first adjusted by bringing the board *E* into the proper position.

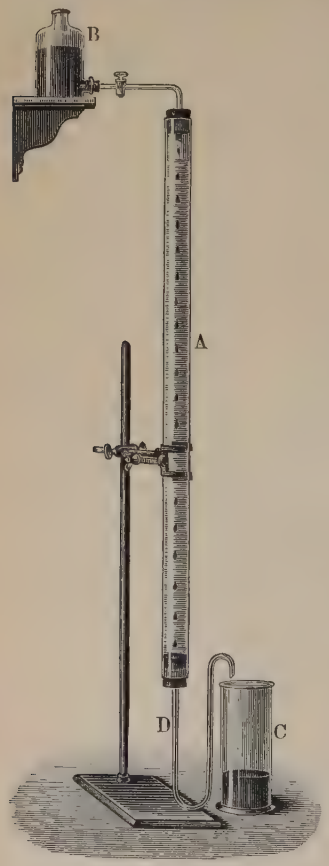

Fig. 37.

Purification of Mercury by Nitric Acid.

Very pure mercury is obtained by letting it fall in small drops through a column of nitric acid about 1 metre high. The arrangement for this purpose is shown in Fig. 37.

A is a glass tube from 2 to 3 cm. wide, and fitted at the lower end with a cork and the bent glass tube *D*. *B* is the supply bottle for impure mercury, and *C* the receiver for the purified mercury. Some pure mercury is first poured into the tube *D*, and *A* is then filled with dilute nitric acid, the acid being kept in the tube by the pressure of the mercury in *D*. Upon allowing the mercury to drop from *B*, the purified metal passes slowly over into *C*.

Purification of Mercury by Air.

According to Crafts, mercury is completely purified by leading air through the metal. Leading air through for forty-eight hours suffices for 20 kg. of mercury. Zinc, copper, and lead are completely changed to oxides. The mercury thus purified does not further change upon exposure to the air.

Berzelius had already noticed[1] that foreign substances may be removed from mercury by shaking it with air. Maumené has used the method for the preparation of mercury for barometers. He put 1 kg. of mercury into a litre bottle and fastened the bottle to the wheel of a wagon. After driving for a few minutes, a dust of the foreign metals, mixed with mercury, was formed.

Remarks upon the Making of Apparatus.

In making apparatus, it is a decided mistake to use tubes which are too thick-walled, for such tubes break of themselves, without other cause, upon being exposed to slight changes of temperature. One should further avoid fastening the apparatus at too many places to the wooden or iron standards. As a rule the glass should be fastened at only a very few points, and even then in such a manner that a free expansion in certain directions is possible. The attachment is best made by fastening a metal band over the glass, but not touching it, and filling the space between the board and the glass with plaster of Paris. If it is

[1] *Chemikerzeitung*, 1888, pp. 741, 808. *Ann. de Chim.* **87**, 144.

necessary to fuse platinum wires in the glass, very fine wire should be used. It is easy to fuse this into the glass absolutely gas-tight without the use of enamel, while thicker wire cannot always be put in perfectly tight even by an expert glass-blower.

CHAPTER VI

ANALYSIS WITH THE USE OF ORDINARY ABSORPTION APPARATUS

Gases which are soluble in water, *e.g.* ammonia, chlorine, sulphur dioxide, etc., are best determined by leading them through a suitable absorption apparatus and ascertaining their amounts by weighing or titration. In doing this it is necessary that the volume of the gases not absorbed be measured by an appropriate apparatus placed either before or behind the absorption apparatus.

This method of analysis is especially well adapted to the determination of very small quantities of a gas.

In analysing a gas mixture by directly determining the volumes of the constituents, all the measurements must be made with the same sharpness; but when the work is done in the manner above mentioned a much less accurate measurement of the total volume suffices, correct results being obtained if only the determination of the gas in question is accurately made.

For example, in determining the carbon dioxide in the air by measuring its volume, if 100 ccm. of air be taken, the measurements must be exact to the hundredths of a cubic centimetre, even if one wishes

only to approximate the accuracy demanded in analyses of the atmosphere. But by using a standardised solution with which the gas is brought into contact, a much greater accuracy may easily be obtained even with relatively rough measurement of the initial volume.

A simple calculation will best make this clear.

Let us suppose that 10 litres of air are taken for the analysis, and that, by titration, 4 ccm. of carbon dioxide are found to be contained therein, *i.e.* 0·04 per cent. Suppose further that a mistake of 10 ccm., which would be an enormous experimental error, has been made in the measurement of the air. The amount of carbon dioxide calculated for an initial volume of 10010 ccm. would be 0·03996 per cent, or for 9990 ccm. 0·04004 per cent.

Let us suppose further that in using burettes which are graduated in fifths, the error in reading is 0·1 per cent; then this would already be $2\frac{1}{2}$ times as great as the amount of CO_2 present.

From this it follows that very small quantities of a gas, mixed with large volumes of other gases, should be determined if possible by absorption and subsequent weighing or titration.

A very suitable apparatus for the absorption of gases is the absorption tube proposed by Pettenkofer (Fig. 38), of which a more convenient form has been devised by Winkler (Fig. 39). If gases only are to be absorbed, the Pettenkofer tube is admirably suited to the purpose. If, however, the gases contain substances in the form of dust, a complete absorption is not obtained; in such cases the gas bubbles must be broken up, this being done by means of a long perpendicular glass tube filled with glass beads. A

convenient device for this purpose is a combination of such a tube with a Peligot tube (Fig. 40).

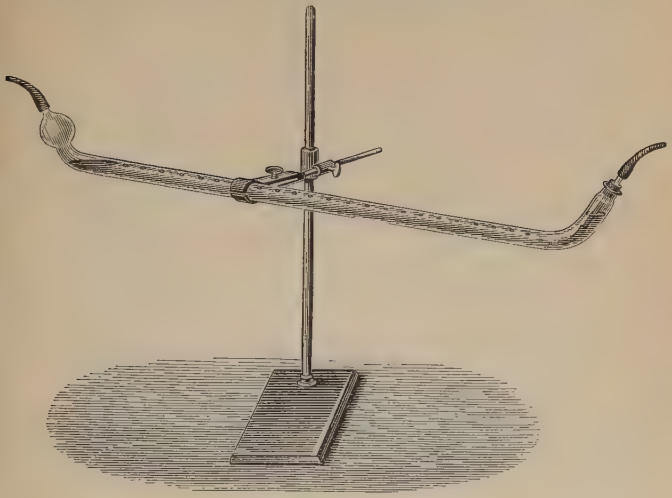

Fig. 38.

If the vessel may be shaken during the absorption, a simple Woulf bottle answers every purpose.

To absorb large amounts of gases the apparatus devised by Winkler may be advantageously used. He obtains a large surface of contact by employing light and porous pumice-stone, and the absorption apparatus he uses has the form shown in Fig. 41. The cylinder

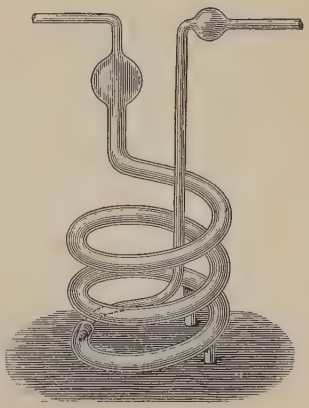

Fig. 39.

a has two openings at the top, and it ends at the bottom in a tube which is ground into the neck of the Woulf bottle *b*. The bottle contains the absorbing liquid, and *a* is filled with pieces of pumice-stone. Upon blowing into *d* the liquid is made to rise, the

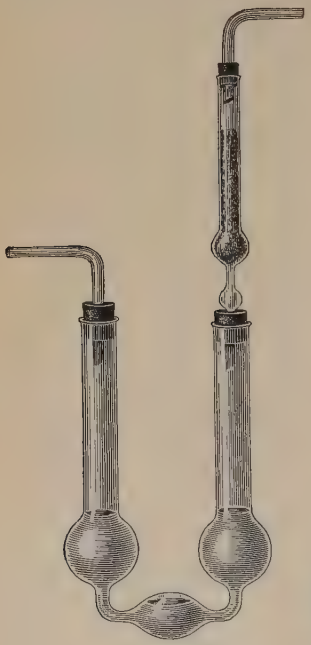

Fig. 40.

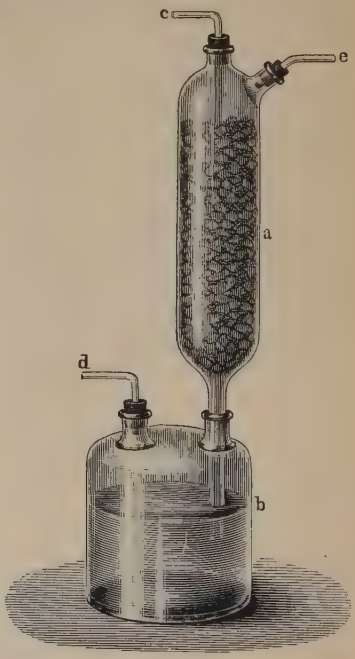

Fig. 41.

pumice-stone becoming thereby thoroughly moistened. Upon reopening *d* the excess of liquid flows back into *b*, and the apparatus is ready for the absorption. The gas enters through the tube *c*, which extends as far as the narrow part of *a*, and then rising through the moistened pumice-stone it passes out at *e*.

Reiset[1] has constructed a very effective absorption apparatus for the determination of carbon dioxide in the atmosphere, this device rendering it possible to work with very large volumes of air (600 litres). The construction is shown in Fig. 42. *I* is a U-tube filled with pieces of pumice-stone moistened with concentrated sulphuric acid. At the lower end of the

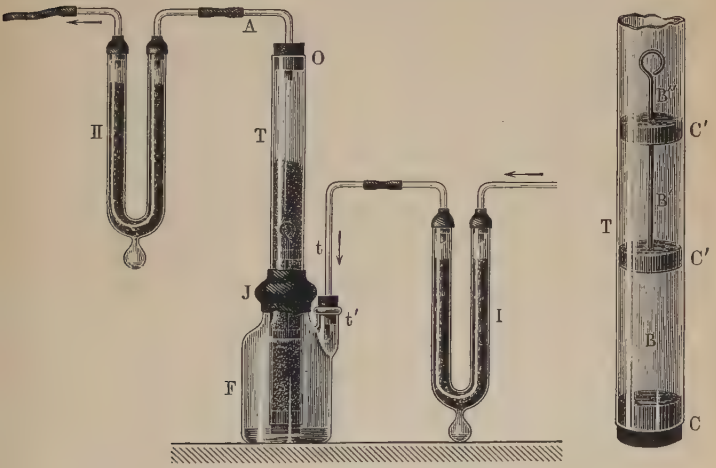

Fig. 42.

tube is a bulb in which collects the dilute sulphuric acid, which would otherwise retard the passage of the air. This tube *I* acts as a drying tube: it holds back the total moisture of the air used in the experiment, and its increase of weight gives the percentage of moisture in the air. The dried gas now passes into the absorption apparatus proper through the tube *t*

[1] *Comptes rendus*, vol. lxxxviii. p. 1007; and vol. xc. p. 1144. *Chemikerzeitung*, **4**, 485.

which is fastened into the neck of the bottle *F*. This part of the apparatus is based upon the principle which Schlösing made use of to absorb the ammonia in the atmosphere, and to facilitate its quantitative determination. Three slightly conical little boxes, *C*, *C'*, and *C''* (Fig. 42), made from thin platinum foil, are pushed into the glass cylinder *T*, the friction with the sides of the tube holding them in place. Each little box has a diameter of 4 cm., and is pierced with 120 holes of about 0·5 mm. diameter. *T* is 0·5 m. long. It is joined to *F* by means of a thick, tightly fitting rubber ring *J*. Before beginning the analysis 300 ccm. of a clear standardised solution of baryta water is put in the tube. The tube is then connected air-tight with the U-tube *II*, which is filled in exactly the same manner as *I*, and the aspirating is begun.

At the end of the experiment, that is, after 600 litres of air had passed through, Reiset found the baryta water in the bottle and in the lowest part *B* of the cylinder completely charged with carbonate, that in *B'* only milky, while the solution in *B''* was clear and transparent—a proof that the carbon dioxide was completely absorbed.

The baryta water is now brought into a bottle supplied with a tightly fitting stopper, and the cylinder and bottle are carefully rinsed with known quantities of water.

The U-tube *II* is weighed, and the amount of water carried over from the baryta water is thus determined. The barium carbonate is allowed to settle, and as the total amount of liquid is now known, a titration of a measured portion of the clear solution gives the amount of unchanged barium hydroxide, and,

by a simple calculation, the per cent of carbon dioxide in the atmosphere. (The measured volume of air is of course always reduced to 0° and 760 mm. pressure.)

For measuring gases a gas-meter or simple aspirator is employed. The measurement can be made very simply by calculating the gas volume from the amount of water which has flowed from the aspirator, with corrections for temperature and barometric pressure.

Fig. 43 shows such an arrangement. *A* is a Pettenkofer tube, *B* is a bottle which can be emptied by the glass siphon *a*, *C* is a graduated bottle. To make a determination, bring an accurately measured amount of reagent into the absorption tube, open the siphon, and measure the quantity of water which passes over, beginning the measurement at that moment when the first bubble passes from *b* into the absorbing liquid.

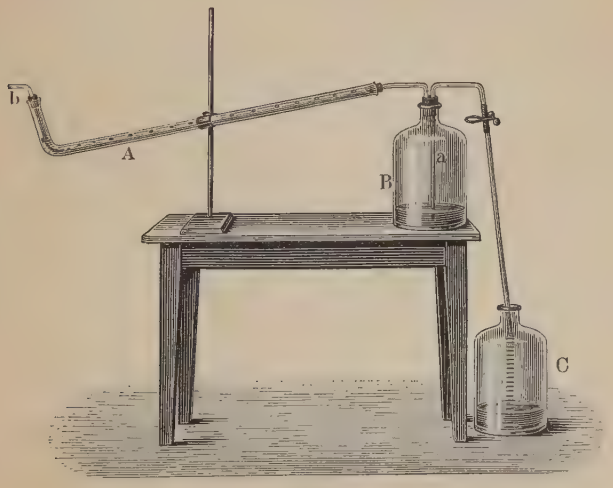

Fig. 43.

PART II

SPECIAL METHODS

CHAPTER I

GENERAL REMARKS UPON ABSORPTION ANALYSES WITH THE APPARATUS FOR TECHNICAL GAS ANALYSIS

The accuracy which may be attained by simple absorptions carried out in the apparatus previously described is so great, even when the analyses are made over aqueous solutions, that it is but slightly inferior to the exact analyses made over mercury, and in all cases completely satisfies the great demands made upon the technical chemist.

For the sake of comparison, two partial analyses by this method and an exact analysis over mercury (see Part I., Chap. III.) are here given: the gas used in each case is illuminating gas, taken September 23d, 1877.

I. Technical Analysis.	II. Technical Analysis.	Exact Analysis over Mercury.	
1·6 per cent	1·5 per cent	1·5 per cent	carbon dioxide
3·1 „	2·9 „	3·0 „	heavy hydrocarbons
1·4 „	1·6 „	1·4 „	oxygen.

Errors so large that they may entirely destroy the value of the analysis result when the apparatus and the reagents do not have the temperature of the

laboratory, or when the temperature changes during the brief time necessary for the analysis. Since, for example, a rise of temperature of only one degree would cause an error of 0·3 per cent in a total volume of 100 ccm., it follows that working near a stove, boiler, fire, etc. is wholly inadmissible, and that the apparatus and confining liquids must be kept at the place where the analysis is made.

It is of no less importance for the obtaining of accurate results that the confining liquids be allowed to flow down from the walls of the burette in exactly the same manner after each absorption. Otherwise an error may be caused by the adhering of more or less liquid to the glass walls. One can easily convince himself by experiment that, with gases confined over water, readings which are made one minute after the gas has been shaken with water in the burette differ by several tenths of a cubic centimetre from readings made five minutes later. With all other liquids, such as caustic alkalies, cuprous chloride, concentrated sulphuric acid, etc., the running-down takes place much more slowly, so that an error of one cubic centimetre or more may result. The condition of the glass plays an important part here, as in all adhesion phenomena. An invisible layer of a salt or fat acts, of course, quite differently from the clear glass surface.

The author has found by repeated experiment that distilled water will run down completely in five minutes, while a 5 per cent solution of sodium hydroxide requires ten minutes, and concentrated sulphuric acid from fifteen to twenty. For this reason, rapid and at the same time accurate work is quite impossible in all those forms of apparatus

in which the gas is not always measured over the same liquid, as it is in the Orsat apparatus, and with the burettes and pipettes here described.

In the method previously given, the gases pass from the pipettes into the measuring burette in nearly equal spaces of time, or in time proportional to the volume of the gases, since the connecting capillary acts as a regulator, and also since the adhesion of the water in the burette does not vary during the analysis. For these reasons the reading may be taken either shortly after the gas has been drawn back into the burette, or after the water has run down, and good results may be obtained in both cases. The most accurate results are naturally obtained from readings taken after the water has run down completely.

Confirmatory Analyses.

Partial analysis of a sample of illuminating gas taken September 13th, 1877.

I. 100 ccm. of gas were taken.

The readings were made five minutes after passing the gas back into the measuring burette; that is, after complete running down of the water.

Results—

2·4	per cent	carbon dioxide
3·4	„	heavy hydrocarbons
0·8	„	oxygen
8·1	„	carbon monoxide.

II. The readings were made one minute after

passing the gas back, the running down of the water not being waited for.

Beginning of the analysis, 10.36 A.M.
End „ „ 11.14 „

Results—

2·0 per cent carbon dioxide
3·3 „ heavy hydrocarbons
0·7 „ oxygen
8·1 „ carbon monoxide.

CHAPTER II

CONCERNING THE SOLUBILITY OF GASES IN THE ABSORBENTS

THERE is no doubt that working with unsaturated absorbing liquids leads to the most erroneous results, and that on account of the variation of temperature and pressure the highest scientific accuracy can be attained only by working over mercury and with solid absorbents. In by far the greater number of cases, however, the use of aqueous solutions is possible if they are allowed to become saturated in the manner mentioned on p. 39.

It would be a decided mistake if, for example, in an analysis of a mixture of carbon dioxide, nitrous oxide, and nitrogen, the absorbing liquid were saturated with nitrous oxide by leading the pure gas through the absorbent, and thus bringing it into contact with the liquid at the pressure of an atmosphere. The error, however, is very small if the absorbent is saturated in such a manner that the amounts of dissolved gases correspond exactly to the partial pressure which the various constituents will exert in the analysis to be made. Although this may not be possible in a theoretical sense, yet in most

cases it may be accomplished to a quite sufficient degree by making, with the same absorbents, two or three analyses of the same gas mixture, one directly after another. It is precisely this consideration which gives the great exactness to the work with the pipettes devised by the author, an exactness which cannot be attained with the simple gas burettes. In the examination of industrial gases, where repeated analyses of nearly identical gas mixtures are made, the pipettes remain of themselves sufficiently saturated, so that a double analysis is generally unnecessary. Parallel analyses, made by the author, over water on the one hand and over mercury on the other, serve to confirm the statement given above.

The determination of carbon monoxide in a gas gave—

With unsaturated reagent—

8·6 and 8·5 per cent ;

With saturated reagent—

8·1 and 8·0 per cent.

Two partial analyses of a sample of illuminating gas taken April 24th, 1879, gave—

With unsaturated confining water—

3·5	per cent	carbon dioxide
4·6	„	heavy hydrocarbons
11·2	„	carbon monoxide ;

With saturated confining water—

3·3	per cent	carbon dioxide
4·6	„	heavy hydrocarbons
10·3	„	carbon monoxide.

Washing out the reagents from the burette with water, as several writers have proposed, is thus quite impracticable, as one may easily convince himself by comparing results so obtained with those given by an exact analysis.

If an analysis need be accurate only to within 0·5 per cent, it is unnecessary to first saturate the confining water with the gas under examination.

Errors much larger than those mentioned above,—so large, in fact, as to give completely misleading results,—arise from faulty arrangement of the apparatus in taking the sample.

CHAPTER III

CONCERNING THE COMBUSTION OF GASES

SINCE absorbents for all gases are not as yet known, the combustion is an operation of great importance.

The heating of the gases to the temperature of combustion is accomplished either from within by an electric spark, the combustion then taking place in an instant as an explosion, or from without by leading the gas through a tube heated from the outside.

By means of the combustion, the nature and volume of the elementary constituents of a single combustible gas of unknown composition and its molecular structure may be determined.

Bunsen has stated the theoretical data in his *Gasometrische Methoden*, 2d edition, 1877, pp. 48-51.

If, in this question, we start with the most complicated case, viz., that in a volume of a gas there are x vol. of gaseous carbon, y vol. hydrogen, z vol. oxygen, and n vol. nitrogen, then four equations are necessary for determining x, y, z, and n. To obtain these four equations it suffices to burn a volume V of the gas in question, and then to determine (1) the contraction C resulting from the combustion ; (2) the aqueous vapour

Y which has been formed; (3) the resulting carbon dioxide X; and (4) the separated nitrogen S.

The gaseous carbon x contained in a unit volume of the gas gives $2x$ carbon dioxide, and V volumes give $2x\mathrm{V}$. Hence

$$\mathrm{X} = 2x\mathrm{V}, \quad \text{or} \quad x = \frac{\mathrm{X}}{2\mathrm{V}}.$$

The hydrogen y contained in one volume of the gas gives y volumes of aqueous vapour, V volumes give $\mathrm{V}y$. Hence

$$\mathrm{Y} = y\mathrm{V}, \quad \text{or} \quad y = \frac{\mathrm{Y}}{\mathrm{V}}.$$

Since, further, in a unit volume of the gas there are n volumes of nitrogen, and in V volumes $\mathrm{V}n$ nitrogen, it follows that

$$\mathrm{S} = \mathrm{V}n, \quad \text{or} \quad n = \frac{\mathrm{S}}{\mathrm{V}}.$$

Finally the volume of gas before the combustion is made up of the gas volume V and the oxygen volume O which has been added. The gas volume remaining after the combustion is equal to the oxygen volume O added, minus the oxygen volume $2x$ necessary to the formation of the carbon dioxide, minus the oxygen volume $\frac{1}{2}y$ necessary for the formation of the water, plus the volume of the carbon dioxide formed $2x$, plus the oxygen volume z contained in the original gas, plus the nitrogen volume n separated from the gases by the combustion. Substituting now the values found for x, y, and n, we have—

As volume before the combustion, $\mathrm{V} + \mathrm{O}$;

As volume after the combustion, $\quad \mathrm{O} - \frac{\mathrm{Y}}{2\mathrm{V}} + z + \frac{\mathrm{S}}{\mathrm{V}}$.

Subtracting the lower expression from the upper, there results, for the gas volume which has disappeared—

$$C = V + \frac{Y}{2V} - z - \frac{S}{V},$$

or $$z = V - C + \frac{Y}{2V} - \frac{S}{V}.$$

To determine V, X, Y, S, and C by experiment, V volumes of the gas under examination are brought into the explosion eudiometer, an amount of oxygen O necessary for the combustion is added, and the mixture then ignited. The reduced gas volume disappearing in the explosion is C.

The eudiometer is now heated to 100° C. in a suitable apparatus. The difference between the reduced volumes before and after the heating is Y.

The volume of carbon dioxide X is next determined by means of a potash ball. The residue now in the eudiometer consists of nitrogen mixed with an unknown amount of oxygen. This latter is determined by combustion with hydrogen, and is subtracted, and the volume of nitrogen is thus found.

If chemical tests show that the gas contains no oxygen, *i.e.* that $z = 0$, then

$$0 = V - C + \frac{Y}{2V} - \frac{S}{V};$$

substituting the value Vy for Y, there results—

$$0 = V + \frac{y}{2} - C - \frac{S}{V}, \quad \text{or} \quad y = 2\left(C + \frac{S}{V} - V\right).$$

With the aid of this equation the hydrogen contained in a unit volume of a gas free from oxygen may be

calculated from the contraction, the direct determination of the volume of aqueous vapour Y being thus rendered unnecessary.

The method holds good for nitrogen, oxygen, hydrogen, and all gases of the following composition:—

n vol. C + n_1 vol. N = 1 vol.
n „ C + n_1 „ O = 1 „
n „ C + n_1 „ H = 1 „
n „ H + n_1 „ O = 1 „
n „ H + n_1 „ N = 1 „
n „ N + n_1 „ O = 1 „

n vol. C + n_1 vol. H + n_2 vol. O = 1 vol.
n „ C + n_1 „ H + n_2 „ N = 1 „
n „ H + n_1 „ O + n_2 „ N = 1 „
n „ C + n_1 „ O + n_2 „ N = 1 „
n „ C + n_1 „ H + n_2 „ O + n_3 „ N = 1 vol.

It is seen that in this list of gases there are some, namely O and n vol. N + n_1 vol. O = 1 vol., which contain no constituent combustible with oxygen. With such gases hydrogen must be added for the combustion instead of oxygen. If V is the initial volume, C the gas volume disappearing in the combustion, and H the hydrogen added, we then have as—

Vol. before the combustion

$$(1)\ V + H$$

and after the combustion the volume will be—

The hydrogen added, minus twice the volume of the oxygen in the gas, plus the remaining nitrogen, or

$$(2)\ H - 2z + n.$$

Subtracting (2) from (1) we get

$$C = V + 2z - n,$$

or $$z = \frac{C - V + n}{2}.$$

It is thus possible on the one hand to determine the molecular constitution of a gas by combustion, while, on the other hand, the quantitative proportions of the various constituents of a gas mixture whose qualitative composition is already known, can of course be ascertained by combustion.

By experiment can be determined—

1. The total contraction caused by the burning of the gases.
2. The water formed in the combustion.
3. The carbon dioxide formed in the combustion.
4. The oxygen used in the combustion.
5. The nitrogen remaining after the combustion.

Five equations may be made from these experimental figures thus derived and from the known combustion relations of the gases; hence, by means of a single combustion of a gas mixture containing five different gases which are qualitatively known, the amounts of these five gases may be determined.

Since we can sharply separate most gases by means of absorbents, the combustion is generally used only for the separation of nitrogen from hydrogen, marsh-gas, and the higher members of the marsh-gas series.

Of especial significance is Bunsen's discovery that nitrogen and oxygen, in very violent explosions, combine directly to form nitric oxide or nitrogen tetroxide and nitric acid. Bunsen found that—

100 vol. of air with 13·45 oxyhydrogen would not burn.

						Vol. of Air remaining.
100	air	burned	with	26·26	oxyhydrogen gas, left	100·02
100	„	„		34·66	„ „	100·15
100	„	„		43·72	„ „	100·07
100	„	„		51·12	„ „	99·98
100	„	„		64·31	„ „	99·90
100	„	„		78·76	„ „	99·43
100	„	„		97·84	„ „	96·92
100	„	„		226·04	„ „	88·56

Bunsen seeks to avoid the inaccuracies which exist in many of the older gasometric results, by never using in his experiments more than 26 to 64 volumes of combustible gas to 100 volumes of incombustible gas.

These figures give us undoubtedly a sharp dividing line, but the author would call attention to the fact that they do not hold good in all cases. The author has ascertained by experiment that the explosion phenomena when marsh-gas and oxygen or carbon monoxide and oxygen are used, are quite different, and call for different proportions of gas.

The gases named give less violent explosions. By following Bunsen's directions the burning of the nitrogen will be always avoided, and the worst that can occur is that the gas mixture is not sufficiently explosive.

By practice one very quickly learns to judge from the appearance of the flame caused by the explosion, as to whether the explosion has been strong enough. For complete combustion it is necessary that an active explosion take place. In incomplete combustion the progress of the flame in the gas mixture can be followed by the eye.

If larger amounts of gas are available, they may be burned by mixing them with air or with oxygen, leading them over heated copper oxide, and weighing the carbon dioxide and water formed. R. Fresenius suggests[1] the use of a combustion tube about 30 cm. long and not too wide, filled, without a canal, with coarse-grained copper oxide. The copper oxide is held closely together by means of stoppers of asbestos, about 7 cm. long, inserted in each end of the tube. The asbestos must first be ignited in moist and then in dry air. The tube is wrapped with wire gauze, and is heated to red heat in a small combustion furnace. The gas and the air or oxygen necessary for the combustion are led over soda-lime or calcium chloride, and it is best to bring them together after they have entered the combustion tube, the gases entering the tube separately through the two openings of a rubber stopper. The gas must previously be accurately measured. The water formed in the combustion is absorbed in a calcium chloride tube, and the carbon dioxide in a Liebig potash bulb.

The combustion may be made in a much simpler manner by explosion in pipettes.

The Explosion Pipette for Technical Gas Analysis (Fig. 44).

This consists of the thick-walled explosion-bulb *a* and the level-bulb *b*, which are joined together by a wrapped piece of rubber tubing. At *c* two fine platinum wires are fused into the explosion pipette, the ends of the wires being about 2 mm. apart. At

[1] *Zeitschrift für analytische Chemie*, **3**, 339.

d is a glass stopcock, and the pipette terminates in the capillary *e*, whose end is closed by a short piece of rubber tubing and a pinchcock. In general the pipettes and burettes for technical gas analysis are filled with aqueous solutions, but the explosion pipette is filled with mercury. By using mercury as confining liquid during the explosion it is possible to afterwards determine the carbon dioxide formed by the com-

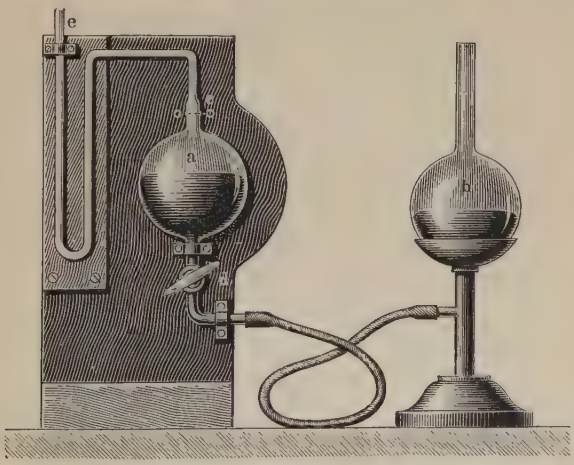

Fig. 44.

bustion. If the explosion is made over water, a subsequent measuring of the carbon dioxide formed is inadmissible, because the pressure in the pipette is so high during the explosion that considerable quantities of carbon dioxide are absorbed by the water. By exploding over mercury very satisfactory results are obtained, even if the carbon dioxide is afterwards measured in a burette which is filled with water.

One is often called upon to analyse gas mixtures

which do not contain sufficient combustible ingredients to make them explosive when mixed with oxygen or air; in such cases combustibility is produced by adding pure hydrogen.

The hydrogen is made in the hydrogen pipette (Fig. 45). This is a double absorption pipette which

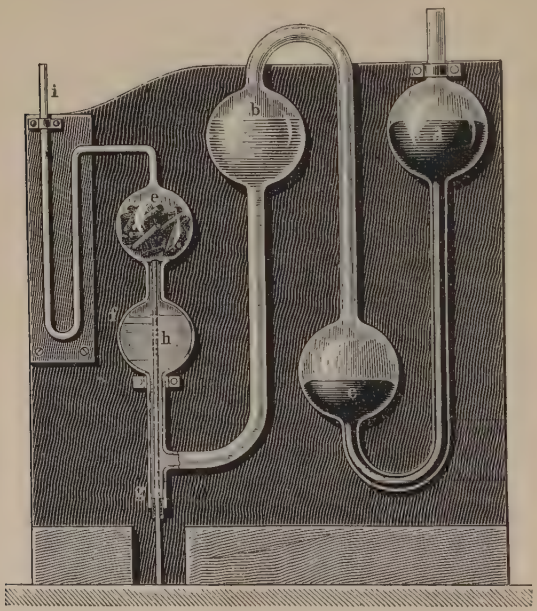

Fig. 45.

has two small bulbs in the place of the first large bulb. Through the tube *g* a glass rod *h* is pushed up to the mouth of *c*. This rod is fastened tightly into *g* by means of a piece of rubber tube slipped over it, and it serves to hold pieces of chemically pure zinc in the bulb *c*. To fill the pipette it is inverted, the glass

rod is taken out, and the pieces of zinc are dropped into *c*. The pipette is then closed again, placed upright, and filled with diluted sulphuric acid (1:10) by means of a funnel with a very long tube attached to the capillary *i*. The hydrogen evolved during the filling frees the sulphuric acid from any absorbed air and at the same time fills the bulbs *b* and *c*. When about 100 ccm. of sulphuric acid have been brought into the pipette, some mercury is poured into *d*. The pipette is closed at *i* with a piece of rubber tubing and a pinchcock.

After a short time the hydrogen produced will drive back the acid, so that the evolution ceases; the mercury prevents the entrance of air into the apparatus, pure hydrogen thus standing ready for use at any time.

It is advisable to force a little water into the capillary tube to prevent the entrance of air at this point; the hydrogen will then remain perfectly pure for months. To obtain a more active evolution of hydrogen than that which takes place when pure zinc and pure acid are used, a few pieces of platinum foil may be put in with the zinc.

The Explosion Pipette for the Apparatus for Exact Analysis (Fig. 46).

In the exact analysis also it is most convenient to make the explosions in a pipette especially constructed for the purpose. This pipette differs from the ordinary pipettes only in having a stopcock at *a* and two platinum wires fused in at *b*.

To burn a gas mixture in this apparatus, the gas is

brought into it in the usual manner, the stopcock is closed, and a fine sewing needle is placed in the mouth of the capillary *c*. Upon connecting the platinum wires with an induction apparatus, the mixture is exploded by the spark which passes when the circuit is closed.

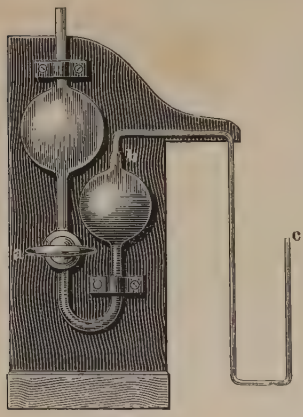

Fig. 46.

Hydrogen is made in the

Hydrogen Pipette (Fig. 47).

Its construction is similar to that of the hydrogen pipette for technical gas analysis.

The most suitable apparatus for the evolution of

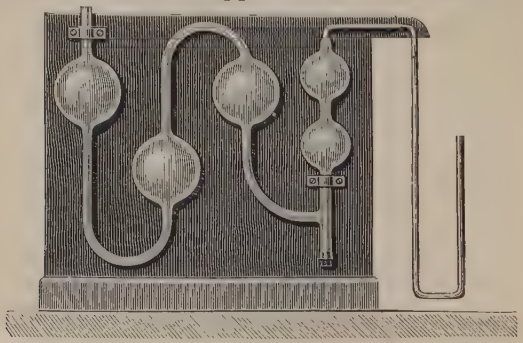
Fig. 47.

oxyhydrogen gas is one closely resembling the Bunsen apparatus.

The Oxyhydrogen Gas Generator.

The author has found that in the evolution of oxyhydrogen gas there is always formed some ozone which, upon being passed through mercury, unites with the metal. For this reason oxyhydrogen gas in which the ozone has not been previously decomposed, leaves a slight residue of hydrogen when one works over mercury. If the oxyhydrogen gas is collected over potassium iodide, iodine is set free even after the evolution has proceeded for some hours. A direct experiment gave 0·7 ccm. of free hydrogen in a litre of the gas. The ozone is removed either by putting the apparatus, during the evolution, into water heated to 90°, or by exposing the oxyhydrogen gas, before using it, to the action of diffused daylight for 12 hours, whereby the ozone disappears of itself. The latter way is the more convenient, and hence in the apparatus, Fig. 48, the bulb *c* of about 50 ccm. capacity is interposed between the delivery tube *b* and the vessel *a*. When the apparatus is put into use, it is filled by a rapid evolution of oxyhydrogen

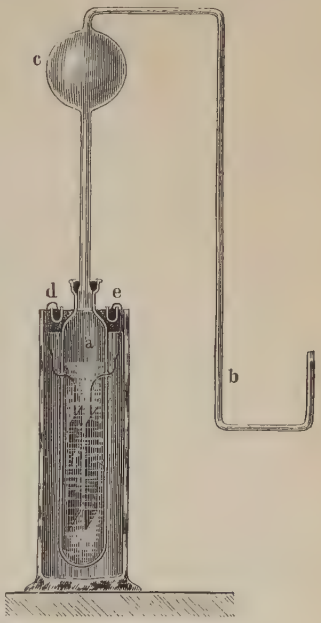

Fig. 48.

gas lasting for $1\frac{1}{2}$ hour, and is then allowed to stand for 12 hours. If inside of 24 hours never more than 40 ccm. of the gas be taken for analysis, one may be sure that only pure oxyhydrogen gas is being employed. To take off a portion of the gas, the delivery tube is brought into the measuring bulb, and by further evolution of the oxyhydrogen gas the desired amount of the same is driven over. The freshly evolved gas containing ozone drives the pure gas before it. Two little glass cups, *d* and *e*, serve as pole contacts. The gas is set free by the plates *f*. A little mercury in the delivery tube at *b* closes the apparatus air-tight.

The Dip Battery.

For producing the electric current, the form of dip battery devised by Bunsen is very convenient (Fig. 49).

In this form the zinc and carbon plates stand opposite one another, and are dipped into a single solution which is prepared as follows[1]: 765 grams of commercial pulverised potassium bichromate, which usually contains about 3 per cent of impurities, is gradually brought into 0·832 litre of sulphuric acid of 1·836 sp. gr., the acid being constantly stirred. When the potassium bichromate has been changed to chromic acid and potassium sulphate, 9·2 litres of water are poured in, in a thin stream, with constant stirring. The mixture, which was already hot, now heats up still more, and the crystals gradually dissolve.

[1] Poggendorff's *Annalen*, 1875, **154**, p. 248.

The above amounts make 10 litres of the battery solution.

If the circuit be closed by a conductor of low

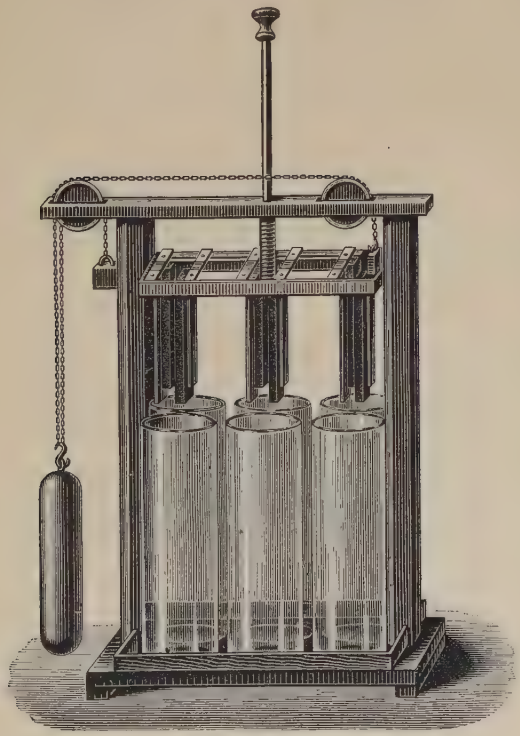

Fig. 49.

resistance, there may be seen in the red solution a dark-coloured column of liquid which, starting from the dissolving zinc plate, sinks to the bottom and collects in the lower part of the glass cell in the form of a rather sharply defined layer.

The original solution has a specific gravity of 1·140, while that charged with the zinc sulphate has a specific gravity of 1·272. Hence the liquid once used sinks to the bottom and is constantly replaced by fresh, unchanged solution. A circulation is thus established which has a considerable influence upon the constancy of the current.

The Induction Coil.

Sparks for the explosion are best obtained by means of a Ruhmkorff inductor. Too small a coil

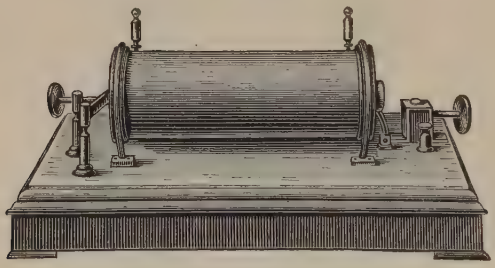

Fig. 50.

should not be chosen, but one about 15 cm. long will be found sufficient. If the induction coil is too small it may easily occur that the spark is too weak to ignite a gas mixture which is but slightly explosive.

CHAPTER IV

PARTICULARS CONCERNING THE DETERMINATIONS OF THE VARIOUS GASES

To obtain accurate analytical results, it is of the greatest importance to know exactly the absorbing power possessed by the reagents when manipulated in the pipettes in the manner already described. For this reason the author has determined this absorbing power, his idea here being that it is not so important to know how much of a gas an absorbent may be able to take up under the most favourable circumstances, but rather to ascertain how much it can absorb with a certain rapidity, so that, in spite of the short duration of the absorption in the pipettes, the completeness of this absorption is guaranteed.

For this purpose a pipette with a very fine capillary tube (Fig. 28) was filled with mercury and 1 ccm. of the reagent. The accurately measured reagent is here confined between two columns of mercury, and is thus completely protected from the air. The pipette was then connected, by means of a piece of rubber tubing and a capillary tube, with a simple gas burette containing the gas under consideration. This gas was

next drawn into the pipette and shaken as long as a rapid absorption took place, several cubic centimetres at the least disappearing in the space of one minute. Since the figures thus experimentally determined give to the reagent an absorbing power much higher than that which could be relied upon in an analysis, they are divided by four, under the presumption that only a fourth of the reagent should be used if there is to be no doubt as to its absorbing power.

Accordingly, 1 ccm. of approximately $33\frac{1}{3}$ per cent caustic potash solution can absorb not merely 40 ccm. of carbon dioxide, as is stated later, but really 160 ccm. The figures thus obtained will be designated as the "analytical absorbing power"; they refer to 1 ccm. of the reagent.

If an accurate account is kept of how much gas the pipette has absorbed, the effectiveness of the reagent remaining in the pipette is always known, and full use of the absorbent can be made without bringing the accuracy of the analyses in question.

Oxygen.

Specific gravity, 1·10521;[1] weight of one litre, 1·43003. Oxygen is but slightly soluble in water. One litre of water absorbs, from atmospheric air, according to L. A. Winkler[2]—

At 16·87° C., 6·84 ccm.
„ 23·64° „ 5·99 „
„ 24·24° „ 5·916 „

[1] Most of these figures are from Landolt and Börnstein's *Physikalisch-chemische Tabellen*. The litre weights are referred to Berlin.

[2] *Berichte der deutschen chemischen Gesellschaft*, 1888, p. 2843.

And of pure oxygen, according to Bunsen—

At 20° C., 28·38 ccm.

One volume of alcohol takes up, according to Carius, at all temperatures between 0° and 24°, 0·28397 volume.

Molten metals take up oxygen with avidity. According to Levol,[1] silver in the fluid condition absorbs about ten times its volume of oxygen and gives it up, with foaming, when gold is added; it also gives it up on simply solidifying, the so-called "spitting" of silver. If silver, melted with access of oxygen, be dropped into water, large bubbles of oxygen are given off by each drop. Cobalt and nickel act similarly.

Oxygen is determined either by combustion with an excess of hydrogen or copper, or by absorption.

In the combustion with hydrogen, $\frac{2}{3}$ of the volume burned consists of hydrogen, and $\frac{1}{3}$ of oxygen. The volume of oxygen present is hence found by dividing by three the decrease in volume resulting from the combustion.

The necessary hydrogen may be made in the apparatus described on pages 104 and 106.

To obtain the greatest accuracy, Bunsen uses hydrogen produced by the electrolysis of water, the positive pole consisting of a zinc wire floating in mercury.[2]

Following Bunsen's procedure, pure oxygen is burned with from three to ten times its volume of hydrogen. If larger amounts are added, the inflam-

[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part I. p. 83.

[2] Bunsen, *Gasometrische Methoden*, 2d ed. p. 80.

mability is destroyed, or what is more to be feared, is partially obstructed. If the gas is poor in oxygen, it is mixed with twice its amount of hydrogen, and if the mixture is still not inflammable, electrolytic oxyhydrogen gas is added until complete combustibility is established. The gases should always be vigorously shaken in the explosion pipette before the combustion.

To make sure that the combustion has not taken place near the limit of inflammability, the experiment must be repeated with a somewhat larger amount of oxyhydrogen gas.

If the two experiments do not agree, then only that one made with the larger amount of combustible gas is to be regarded as correct. With some experience, however, one can easily tell from the strength of the explosion whether the proportion of combustible to incombustible gas was such that a complete combustion must have taken place.

Very accurate determinations of oxygen may be made by combustion with copper. U. G. Kreusler has so improved the apparatus devised by Ph. v. Jolly for the determination of oxygen in the atmosphere that it is now one of the most exact methods known. A so-called copper eudiometer whose construction is based upon his well-known air thermometer is used for the determination. The air whose oxygen contents is to be determined is admitted into a bulb which has previously been completely exhausted, and the pressure is read off on a very exact mercury manometer. The oxygen is then absorbed by a copper spiral that is heated to glowing by a strong electric current; the metallic copper is changed to cuprous and cupric oxide. After the apparatus has become perfectly cool,

the remaining nitrogen is brought to the initial volume by changing the pressure, and a reading is taken of the pressure now prevailing.[1] When due regard is given to all the necessary precautions, the method is of the greatest exactness; it is, however, very complex and tedious, and for this reason is not well suited to the making of a large number of determinations.

When oxygen is mixed with combustible gases it is necessary to determine it by absorption.

With absorbents a very rapid and, with the use of the necessary precautions, a very accurate determination of oxygen may be made. Good absorbents for oxygen are—

1. A strongly alkaline solution of pyrogallic acid.
2. Chromous chloride.
3. Phosphorus.
4. Metallic copper.

1. *Potassium Pyrogallate.*

The solution of potassium pyrogallate is prepared by mixing together, either directly in the absorption pipette or in the apparatus to be described later, 5 gr. of pyrogallic acid dissolved in 15 ccm. of water, and 120 grams of potassium hydroxide dissolved in 80 ccm. of water.

Especial attention must be called to the fact that caustic potash purified with alcohol should not be used, since this preparation, even after quite strong ignition, may cause erroneous results in the analysis.

[1] U. Kreusler, *Ueber den Sauerstoffgehalt der atmosphärischen Luft. Landwirthschaftliche Jahrbücher*, 1885, p. 305.

The absorptions should not be carried on at a temperature under 15°, for it has been observed that the potassium pyrogallate used for absorption is very much less active at a temperature under 7°. At a temperature of 15° or higher, the last trace of oxygen can be removed with certainty in the space of three minutes by shaking with the solution of potassium pyrogallate, while at lower temperatures the absorption was not complete after six minutes; moreover, the liquid began to foam, and this, in exact determinations, is very troublesome.

A solution prepared as above gave off no carbon monoxide during the absorption, or at the most only such slight traces that the error thus caused came within the limit of error of the readings.

To ascertain how great the error is which can be caused by the evolution of carbon monoxide, the author's assistant, Herr Oettel, in Dresden, and Herren Kreusler and Tacke, in Bonn, analysed samples of air which were collected by Kreusler in Bonn, and sent to Dresden in bulbs sealed by fusion.

The results were as follows:—

	Analysed by Oettel with Potassium Pyrogallate.	Analysed by Tacke by Combustion with Hydrogen.	Analysed by Kreusler with Copper Eudiometer.
Sample of May 4th, 1886.	20·93 per cent oxygen	20·933 per cent oxygen	20·904 per cent oxygen + carbon dioxide
	20·93 ,, ,,	20·901 ,, ,,	20·931 ,, ,, + ,,
Mean :	20·93 per cent oxygen	20·917 per cent oxygen	20·913 ,, ,, + ,,
			20·916 per cent oxygen.
Sample of May 10th, 1886.	20·92 per cent oxygen	20·899 per cent oxygen	20·933 per cent oxygen + carbon dioxide
	20·93 ,, ,,	20·865 ,, ,,	20·919 ,, ,, + ,,
Mean :	20·925 per cent oxygen	20·882 per cent oxygen	20·923 ,, ,, + ,,
			20·925 per cent oxygen.
Sample of May 12th, 1886.	20·92 per cent oxygen	20·935 per cent oxygen	20·928 per cent oxygen + carbon dioxide
	20·92 ,, ,,	20·919 ,, ,,	20·914 ,, ,, + ,,
Mean :	20·92 per cent oxygen	20·927 per cent oxygen	20·935 ,, ,, + ,,
			20·926 per cent oxygen.

These results show that determinations made with the copper eudiometer differ from one another by two to three hundredths of a per cent; the same is also true of the analyses made with the hydrogen eudiometer. The pyrogallic acid method is the most rapid and gives the best agreeing results, so that it appears to be especially suited for parallel analyses.

In technical analysis this solution is used in the double pipette (Fig. 22); in exact analysis in an ordinary pipette (Fig. 28). To effect the absorption, the gas is shaken for three minutes with the solution. The absorption proceeds somewhat slowly, and for this reason the pipette shown in Fig. 23 cannot be used. To obtain accurate results a shaking of three minutes is absolutely necessary. The analytical absorbing power of the solution is from 2 to $2\frac{1}{4}$.

If a large number of oxygen determinations are to be made by the "exact" method, the reagent is kept in the apparatus shown in Fig. 51. With this apparatus a large quantity of the reagent may be kept, measured off, and transferred to the absorption pipettes without ever coming in contact with the air.

The large reservoir bulb *A* ends above in the U-shaped tube *B*, which has a short side-arm at *f* and ends in the ⊢-shaped capillary *g*. To the lower side of the bulb is attached the bent tube *h*, which is provided with a glass stopcock *i*. A small funnel can be fastened to the upper end of *h* by a rubber tube *k*. A thin rubber tube connects the side-arm *f* with the funnel *o*. The ends of the ⊢ capillary *g* are provided with short pieces of rubber tubing and with pinchcocks. The apparatus is first filled completely

with mercury. A funnel or glass tube is then inserted in the free end of *m*, the pinchcocks *n* and *y* are closed, the stopcock *i* is opened, and the aqueous

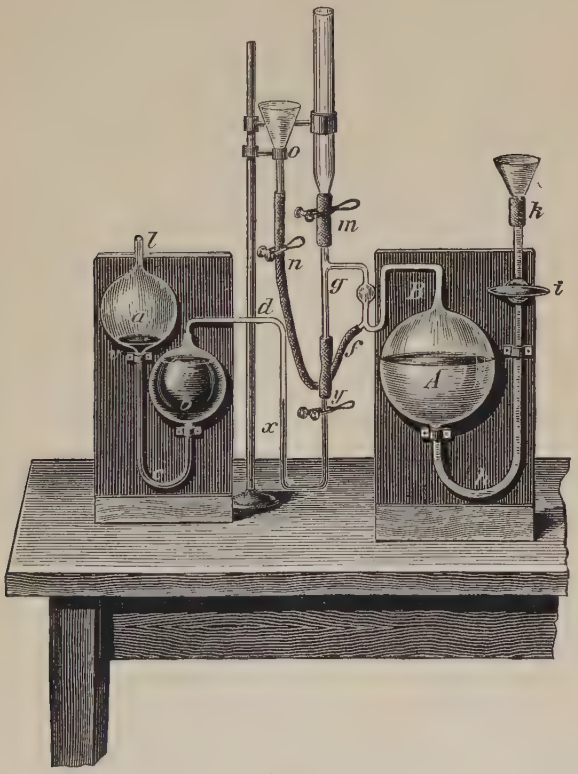

Fig. 51.

solution of pyrogallic acid is poured into the funnel attached to *m*. The end *k* of the tube *h* is now connected by a rubber tube with a suction flask, and the flask is joined to an aspirator. Upon opening

the pinchcock at m the mercury flows through h into the flask, and the solution of pyrogallic acid is drawn into A. The entrance of the reagent can be instantly stopped by turning the stopcock i. When all of the pyrogallic acid has entered the pipette, the solution of potassium hydroxide is poured into the funnel and drawn in in the same manner. The two solutions in the apparatus are then thoroughly mixed by shaking.

To transfer some of the reagent to a pipette, the apparatus is arranged as shown in Fig. 51. The capillary of the pipette is inserted at y into the end of the rubber tube attached to the lower end of g. By blowing into l (this can be best done with the rubber pump, Fig. 11) the mercury in the pipette is driven to g, and m, n, and y are then closed. Some mercury is poured into the funnel inserted in k, and i is opened. Upon lowering the funnel o and opening the pinchcock n, the left side of the U-shaped tube B can easily be filled down to a mark with the reagent, for the mercury drives the reagent out of the bulb into B. When the reagent has been thus measured off, i is closed, y is opened, and by raising the funnel o the reagent is driven over into the pipette until the mercury reaches the point x. The pipette is then disconnected, the capillary d is immersed in a beaker of distilled water, and by careful alternate sucking and blowing at l the capillary is freed within and without from the last traces of the reagent. It is then dried with filter paper, and the pipette is ready for use.

2. *Chromous Chloride.*

Chromous chloride also may be used for absorbing

oxygen.[1] The fact that this reaction is not influenced by hydrogen sulphide or carbon dioxide is further a great advantage. These two gases are completely indifferent to both the blue chromic chloride and the green chromous chloride solutions.

Chromous chloride is the only absorbent that will absorb the oxygen alone in a mixture of oxygen and hydrogen sulphide.

To prepare chromous chloride, von der Pfordten has used the method given by Moissan. A green solution of chromic chloride free from chlorine is made by heating chromic acid with concentrated hydrochloric acid, and this solution is then reduced with zinc and hydrochloric acid. Since spongy particles always separate from the zinc used for the reduction, the solution must be filtered. For this purpose the reduction is carried on in a flask fitted with a long and a short tube, as is a wash-bottle. The longer tube is bent downward above the flask and is here supplied with a small bulb-tube, which is filled with glass-wool or asbestos. The hydrogen given off during the reduction is allowed to pass out through the longer tube for some time; then after closing its outer end the tube is pushed down into the solution. The hydrogen is thus obliged to pass out through the shorter tube, which carries a rubber valve. Carbon dioxide is then passed into the flask through the short tube, and the chromous chloride solution is driven over into a beaker containing a saturated solution of sodium acetate; a red precipitate of chromium acetate is formed which is washed by decantation with water containing carbonic acid. The

[1] Otto von der Pfordten, Liebig's *Annalen*, **228**, p. 112.

red chromium acetate is, relatively speaking, quite unchangeable, and in moist condition it may be kept for an unlimited time in closed bottles filled with carbon dioxide.

In washing the red precipitate some free acetic acid is added in the beginning, to dissolve any basic zinc carbonate which may have been thrown down. In this way a preparation completely free from zinc is obtained.

To absorb oxygen, the chromium acetate is decomposed by the addition of hydrochloric acid, the air being excluded. It is advisable to use an excess of chromium acetate in order to avoid the presence of free hydrochloric acid.

3. *Phosphorus.*

The absorption of oxygen with phosphorus, as described by Lindemann, is much more convenient than the two preceding methods. To obtain the phosphorus in the necessary stick form, it is melted under water in a test-tube placed in a water bath. Enough phosphorus is used to form a column about 6 cm. high. A slightly conical glass tube of 2 to 3 mm. internal diameter is then dipped into the molten phosphorus, the upper end of the tube is closed with the finger, and the tube is lifted out and dipped immediately into a tall beaker full of water. A peculiar movement takes place in the phosphorus enclosed in the tube at the moment when it solidifies, and since the phosphorus undergoes a marked decrease of volume when it becomes solid, the stick usually falls out of the tube upon

gentle tapping; if it adheres, it can easily be pushed out with a wire.

These phosphorus sticks are used in the absorption pipette for solid and liquid reagents (Fig. 21): the cylindrical part is filled as full as possible with the sticks, the remaining space being filled with distilled water.

To make the absorption, the gas whose oxygen contents is to be determined is driven over into the pipette, thereby displacing the water and coming into contact with the moist sticks of phosphorus. A bright glow is visible when the reaction proceeds normally; the phosphorus burns to phosphoric acid, phosphorous acid, etc., at the expense of the oxygen. After three minutes, at the longest, the absorption is complete. The end of the absorption is sharply shown by the disappearance of the glow when the pipette is in a dark room.

Since the different oxidation products of phosphorus are all soluble in water, the surface of the sticks of phosphorus is kept fresh by the action of the confining water alone, if that be renewed from time to time. And further, since these oxidation products, as solid and liquid substances, have a very small tension, no error is caused by the white cloud which may be present in the gas residue after the absorption. The phosphorus can of course be used for a very large number of analyses, if it is protected from the action of the light. To do this the cylindrical part of the pipette is covered with a small box, or the whole pipette is covered, when not in use, by a light-tight box of wood or cardboard.

Parallel analyses showed that the absorption with

phosphorus is very complete, and hence this Lindemann process for the determination of oxygen must be classed among the finest of gas analytic methods, it being of especial value because with one filling of the pipette enormous quantities of oxygen may be absorbed, while potassium pyrogallate possesses a relatively small absorbing power.

Naturally the method cannot be used under those conditions in which phosphorus is no longer able to unite with oxygen. Detailed experiments have been made upon this point by Schönbein in his researches upon ozone. He states that the reaction is entirely or partly prevented by the presence of ethylene ($\frac{1}{4000}$ volume of ethylene is sufficient) and other hydrocarbons or ethereal oils, alcohol, and traces of ammonia.

Moreover, oxygen does not act upon phosphorus when the gas has a very large partial pressure. If phosphorus be brought into contact with oxygen of the density of the atmosphere, no reaction whatever takes place, and not the least light is seen. If, however, the oxygen be diluted with another gas, or mechanically by the air-pump, the reaction begins when the gas has been brought to about 75 per cent of its initial partial pressure. At first a feeble glow is seen, and then suddenly, with a sort of explosive flash of light, the oxygen *burns*, the phosphorus being partly melted.

The reaction takes place normally in gases which do not contain more than 50 per cent of oxygen. To investigate gases which are rich in oxygen, it is advisable to dilute them with an equal volume of nitrogen made from air by absorbing the oxygen with phosphorus.

The reaction is further dependent upon the temperature.

It proceeds normally at about 20° C., while at 14° it takes place quite slowly, so that a quarter of an hour or longer is required to completely separate the oxygen from 100 ccm. of air. At 10° and still lower temperatures a half hour's time would not be sufficient. It follows from this that during the colder months of the year the absorption must be carried out in warmed rooms.

4. *Copper.*

Copper at a red heat or at ordinary temperatures may be used for the absorption of oxygen.

The method of Jolly, in which a copper wire is electrically heated to glowing, has been mentioned above. Copper powder made by reducing granular copper oxide with hydrogen may also be employed. If a hard glass tube, filled with this powder, be heated to red heat in a combustion furnace and the gases be then led through the tube, they can in this manner be completely freed from oxygen.

A very active absorbent for oxygen is metallic copper in the form of little rolls of wire-gauze, immersed in a solution of ammonia and ammonium carbonate.

It has long been known that many metals oxidise readily in the presence of vapour of ammonia. The absorption of oxygen, however, takes place rapidly only so long as the metallic surface is bright, and it proceeds very slowly as soon as considerable quantities of oxide are formed.

By the admirable researches which C. Schnabel has made upon the solubility of the oxides of zinc, copper, etc. in ammonium carbonate, in connection with his work upon the desilverisation of lead by zinc,[1] the author was led to make experiments to see whether it might not be possible to effect a complete absorption by using ammonium carbonate as a solvent for the oxides formed. Experiments showed that oxygen is completely and quickly absorbed when brought into contact with copper and a solution of commercial ammonium carbonate, but that at the same time not inconsiderable quantities of carbon dioxide are given off. When zinc was used, a simultaneous evolution of hydrogen took place, and iron proved to be very slow in its action, as was to be expected from the insolubility of its oxide. Further experiment showed that a very rapid and complete absorption of oxygen results, without any other gas being at the same time given off, when the oxygen is brought into contact with metallic copper and a solution consisting of equal parts of a saturated solution of pieces of commercial ammonium sesquicarbonate, and a solution of ammonia of 0·93 specific gravity. Such an ammoniacal solution has a tension which may in most cases be disregarded, and, provided that the absorption apparatus contains sufficient metallic copper, the solution can easily absorb 24 times its volume of oxygen. Hence its analytical absorbing power is 6.

The reagent is used in the same manner as phosphorus, in a pipette for solid absorbents. In

[1] *Zeitschrift für das Berg-, Hütten- und Salinenwesen im preussischen Staate*, 28.

making the absorption, the gas is allowed to remain in the pipette for five minutes.

The method described admits of a very rapid and exact determination of oxygen, and is to be preferred to the ordinary methods with potassium pyrogallate and phosphorus, provided that the gases do not contain carbon monoxide. As compared with potassium pyrogallate copper has a much greater absorbing power for oxygen, and it has the advantage over phosphorus, aside from the danger attending the use of the latter, of absorbing equally well at any temperature, while the absorption of oxygen by phosphorus takes place very slowly at temperatures below 14° C. Direct experiments showed that, at a temperature of −7° C., the absorption of oxygen in the air was complete in five minutes.

In the analysis of gas mixtures which contain carbon monoxide the method cannot be used, because the basic ammonium cuprous carbonate, formed from the copper present, absorbs carbon monoxide.

Ozone.

A large number of reagents may be used for the detection of ozone. For the detection of such small amounts of ozone as are present in the atmosphere, so-called ozone papers are employed.

Houzeau has suggested that this be prepared by dipping strips of Swedish filter paper into a wine-red litmus solution which contains in a cubic centimetre about 0·013 gram of the extracted constituents dried at 100°; the paper is dried and then impregnated to a fourth of its length with a one per cent solu-

tion of neutral and pure potassium iodide free from iodate. The dried paper must be protected from the air, and is on this account kept in tightly closed bottles.

This paper is coloured slightly blue by from 0·0002 to 0·0003 mg. of ozone. In air containing $\frac{1}{261000}$ of its weight of ozone, the paper turns blue at once. The part of the paper which is coloured with the litmus solution and is not impregnated with the potassium iodide, serves to show the presence in the air of acid or alkaline substances which might influence the reaction. By the action of ozone the potassium iodide is decomposed and potassium hydroxide is formed, which turns the litmus paper blue. Chlorine, nitric acid, and other acid substances do not of course turn the paper blue: in this respect it is superior to those which follow.

According to Schönbein, strips of paper are saturated with a dilute starch and potassium iodide solution (1 KI + 10 starch + 200 water), and these strips are exposed to the air. A distinction of ten shades from white to dark blue is made.

Wurster[1] uses tetra-methyl-para-phenylene-diamene, which, upon taking up one atom of oxygen, is quantitatively oxidised to a blue colouring matter, and by further union with six oxygen atoms changes to a colourless substance. At Wurster's suggestion, Dr. Schuchardt in Görlitz has made a colour scale containing eight numbers. These are obtained by the action of one or two drops of standard iodine solutions upon the tetra-paper:—

[1] *Berichte der deutsch. chemischen Gesellschaft*, 1888, p. 921.

The normal iodine solutions correspond to the numbers on the colour scale . . .	$\frac{1}{250}$	$\frac{1}{500}$	$\frac{1}{1000}$	$\frac{1}{2500}$	$\frac{1}{5000}$	$\frac{1}{10000}$	$\frac{1}{33000}$	$\frac{1}{100000}$
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
And hence contain milligrams of active oxygen in the litre . . .	32	16	8	3·2	1·6	0·8	0·24	0·08

Or, if 16,000 drops are reckoned to the litre :—

	I.	II.	III.	IV.	V.	VI.
Milligrams active oxygen in a drop . .	0·002	0·001	0·0005	0·0002	0·00001	0·000005
	VII.		VIII.			
	0·0000015		0·0000005			

To detect ozone, the paper prepared by one of the foregoing methods is fastened over the end of a glass tube by means of a rubber band, and a measured quantity of gas is drawn through the tube by an aspirator.

With all these papers a blue coloration may be caused by hydrogen peroxide as well as by ozone.

To determine larger amounts of ozone it is best to lead the gas through a solution of potassium iodide and to titrate the iodine set free with a solution of sodium thiosulphate.

The reaction is the following :—

$$O_3 + 2KI + H_2O = O_2 + 2KOH + I_2.$$

As absorbent either cinnamon oil or turpentine oil may be employed : these take up the ozone completely, and are able to absorb very large amounts of the gas.

Especial attention should be called to the fact that rubber is very strongly attacked by ozone. When the gas is to be led some distance, the bell connection

(Fig. 52) devised by Engler and Nasse is well adapted for making the connections. *a* is a bent glass tube over whose end a wide glass tube is fitted by means of a cork *c*. The little cup thus formed is filled with mercury, into which dips the bell *b*.

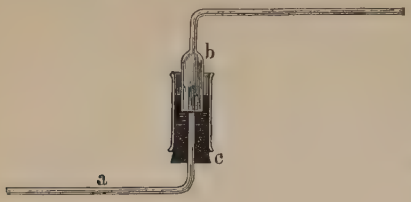

Fig. 52.

To separate ozone from hydrogen peroxide, a bright piece of silver-foil is used: this, as Schöne has discovered, is blackened by ozone, but is not acted upon by hydrogen peroxide.

Nitrogen.

Specific gravity, 0·97010. Weight of one litre, 1·25523. Nitrogen is but slightly soluble in water, one volume of water absorbing, according to Bunsen, at 760 mm. pressure and $t°$,

$0{\cdot}020346 - 0{\cdot}00053887t + 0{\cdot}000011156t^2$ vol. of nitrogen:

hence at

5°, 0·01794 vol.
10°, 0·01607 „
15°, 0·01478 „
20°, 0·01403 „

According to Carius, 1 vol. alcohol takes up at $t°$,

$0{\cdot}126338 - 0{\cdot}000418t + 0{\cdot}000006t^2$ vol. of nitrogen:

hence at

20°, 0·122378 vol.

Up to the present time no method of directly

determining nitrogen is known. The residue of gas mixtures, which cannot be directly determined, is hence calculated as nitrogen. It follows from this that all the errors of the preceding determinations fall upon the nitrogen, and the more complicated the gas mixture the more inexact are the results.

Hydrogen.

Specific gravity, 0·069234. Weight of one litre, 0·089582.

According to L. W. Winkler,[1] one volume of water absorbs at

0°, 0·02148 vol. hydrogen
5°, 0·02044 „
10°, 0·01955 „
15°, 0·01883 „
20°, 0·01819 „

At $t°$ alcohol takes up—

$$0{\cdot}06925 - 0{\cdot}0001487t + 0{\cdot}000001t^2 \text{ vol. of hydrogen:}$$

hence at

20°, 0·066676 vol. (Bunsen).

Hydrogen can be very exactly determined by burning it with oxygen. Either air is used, or, as proposed by Bunsen, pure oxygen made in retorts blown from a glass tube, and of from 6 to 10 ccm. capacity (Fig. 53). These retorts are half filled with dried and pulverised potassium chlorate, and the

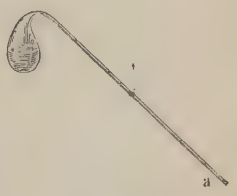

Fig. 53.

[1] *Berichte der deutsch. chem. Gesellschaft*, **24**, p. 89. See also Timofejew, *Zeitschr. für phys. Chem.* **6**, p. 141.

end of the delivery tube is then heated at *a* and bent upwards. The air is first driven out by a rapid evolution of oxygen, and the gas is then led directly into the eudiometer, care being taken that the volume of oxygen does not amount to more than three or four times that of the hydrogen to be determined.

The quantity of hydrogen present is $\frac{2}{3}$ of the volume disappearing in the combustion. If the mixture contains absorbable constituents also, these are first absorbed and the residual gas is then used for the analysis.

When nitrogen is present a considerable error may be caused by not avoiding, in the combustion, the temperature at which nitric acid is formed. Hence one should never neglect to calculate, after the experiment, the proportion of nitrogen to the oxyhydrogen gas burned. If this was less than 6 to 1, the analysis must be repeated with the addition of so much air that this proportion or a still greater amount of nitrogen will be present.

If, on the other hand, the proportion of hydrogen to incombustible gas be very small, such an amount of electrolytic oxyhydrogen gas is added that complete combustion will result. The oxyhydrogen gas disappears completely in the combustion, and hence need not be exactly measured.

An accurately measured amount of pure hydrogen mixed with an excess of air may be used instead of the oxyhydrogen gas. The contraction resulting from the hydrogen added must then be allowed for.

The combustion is made either in the explosion pipette by ignition with an electric spark, or in a glass tube filled with palladium-black, or, as Winkler

has proposed, with palladium asbestos. The advantage of the combustion with palladium is, that in a mixture of hydrogen, marsh-gas, and nitrogen, the hydrogen alone may be burned: this is known as fractional combustion.

Fractional Combustion.

The possibility of separating gases from one another by fractional combustion was first observed by W. Henry, and used by him for the analysis of gas mixtures.

Henry states [1] that carbon monoxide and hydrogen can be removed by combustion from a mixture of hydrogen, carbon monoxide, marsh-gas, and nitrogen by leading these gases over platinum sponge heated to 177°.

Since no convenient method for carrying out this reaction was devised, it had not been adopted into gas analysis.

While studying the occlusion of hydrogen by palladium, the author succeeded in working out a method [2] by which the hydrogen in a mixture with marsh-gas and nitrogen may be fractionally burned in a very short time at the temperature of the room.

The following points concerning the fractional combustion were determined:—

1. A mixture of hydrogen with oxygen in excess, led over palladium sponge which has been superficially oxidised by heating it to redness and allowing it to slowly cool, is completely burned. The reaction

[1] *Annals of Philosophy*, **25**, 428.
[2] *Berichte der deutsch. chemischen Gesellschaft*, 1879, p. 1006.

begins at the temperature of the room, and so much heat is developed that the palladium begins to glow and the gases explode if they are present in the proper proportions to form oxyhydrogen gas.

2. Marsh-gas, mixed with oxygen, and led over palladium, does not burn at temperatures up to 100°: the combustion begins at about 200°. A mixture of 29·3 ccm. marsh-gas and 70·6 ccm. oxygen, led several times over palladium heated to from 200° to 220°, underwent a contraction of 3 ccm.

3. Mixtures of hydrogen, marsh-gas, and oxygen, in the proportions necessary for combustion, often explode very violently when brought into contact with palladium; the author did not succeed in preventing the explosion with certainty, even by the interposition of cooling metals and by the use of thin tubes standing in water.

4. If mixtures of hydrogen, marsh-gas, and air, oxygen being present in excess, be led over palladium at ordinary temperatures up to 100°, the hydrogen alone burns, and the marsh-gas is not at all acted upon, provided that the palladium is not allowed to heat up too much during the reaction. No explosion takes place here.

If the water formed in the combustion is driven off from time to time by heating the palladium upon the cover of a platinum crucible, the palladium does not then need to be regenerated after each experiment, but may be used as it is for a large number of combustions. Since the palladium plays only an intermediary *rôle*, a very small amount of it suffices.

In the following researches 0·5 gram of the metal was placed in a U-shaped glass tube (Fig. 54), which

by means of two capillary tubes *E* was connected on the one side with a gas burette, and on the other with a gas pipette filled with water. The U-shaped tube was kept cool by immersing it in a beaker glass containing water of the temperature of the room. The gases were led through so slowly that the metal either did not glow at all or was heated to redness at some points for only a very short time. A single passage of the gas mixture through the palladium sufficed usually for complete combustion.

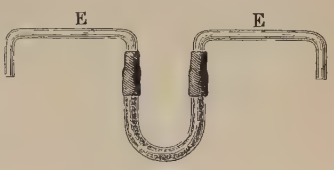

Fig. 54.

Composition of the Gas Mixture.			Resulting Contraction.	Hydrogen calculated from the Contraction.
Hydrogen.	Marsh-Gas.	Air.		
1·5	12	85·1	2·3	1·5
3	8·3	86·5	4·5	3
5·1	12·3	86	7·6	5
9·3	7·1	83·7	14·1	9·4
13·7	7·3	77·5	20·3	13·5
14·1	5·4	81·2	21·2	14·1
14·6	4·5	80·6	22·1	14·7
13·1	6	80·3	19·7	13·1

In the last experiment the palladium tube stood in water at 100°.

From these experiments it follows that, with the addition of air, the hydrogen in any mixture of hydrogen, marsh-gas, and nitrogen may be determined

by fractional combustion at about 100°. For mixtures which, like all furnace or generator gases, contain large amounts of nitrogen, pure oxygen also may be employed.

Cl. Winkler has later suggested that, in place of the tube filled with palladium-black, a capillary tube be used, which contains a very small quantity of palladium asbestos, and which is heated from without by a little flame to the temperature of the reaction. If hydrogen alone is to be burned, this arrangement is quite suitable; if, however, a fractional combustion is to be made, the author prefers the arrangement described above, since with direct heating it is difficult to control the temperature. If the temperature rises beyond 200°, a part of the marsh-gas is burned with the hydrogen. If, however, the palladium tube stands in hot water, the temperature easily regulates itself.

Hydrogen may also be determined by absorption with palladium, potassium, or sodium.

Absorption of Hydrogen by Palladium.

Many endeavours to find an absorption method for separating hydrogen from other gases led the author to ascertain the conditions under which the property of palladium of condensing large amounts of hydrogen at 100°, known as occlusion, may be used for quantitatively separating hydrogen from marsh-gas and nitrogen, as well as from some other gases.

Concerning the purely chemical relations between hydrogen and palladium, a large number of experiments have shown the author—

1. That, on the one hand, palladium loses, as is well known, its silver-white metallic colour when heated nearly to a red heat in the presence of oxygen, and becomes superficially covered with a thin layer of palladious oxide, and that this palladious oxide is, on the other hand, able to burn hydrogen at ordinary temperatures with evolution of heat, so that the intermixed or reduced metallic palladium reaches the temperature at which it can absorb large quantities of hydrogen by occlusion.

2. That the hydrogen taken up by occlusion may be completely removed either by heating the palladium in a vacuum to 100°, or by leading air over the metal at ordinary temperatures. This latter was proved by saturating palladium with hydrogen to the fullest extent possible, by placing the metal in a red-hot tube and leading dry hydrogen over it, and then letting it slowly cool in the current of hydrogen. Air having been led over the palladium thus prepared, the metal was placed in a porcelain tube connected with a Töpler air-pump, and the tube was raised to bright red heat, but no further trace of hydrogen could be obtained.

3. That upon leading air over palladium which had occluded large quantities of hydrogen, the temperature of the metal is raised so high by the combustion that palladious oxide is again formed.

A mixture of hydrogen, marsh-gas, and nitrogen is indifferent to pure metallic palladium, but a strong reaction takes place when the gases are brought into contact with palladium sponge which has been covered with a very thin layer of palladious oxide by heating it to glowing and letting it cool not too rapidly. The

palladium becomes warm and the hydrogen disappears completely, provided the gas is brought into sufficiently intimate contact with the palladium. If air be led over the palladium after the completion of the reaction, which is clearly indicated by the cooling of the metal, the hydrogen in the metal burns and the surface is again covered with palladious oxide. The palladium thus regenerated with air is at once ready for a new absorption; with a few (2·5) grams of palladium sponge in a glass tube an unlimited number of absorptions may be made without the aid of external heat. The reaction concerned is partly combustion, partly occlusion.

What has just been said holds true only when the gases are mixed in certain proportions, since of course the conditions for the regeneration of the palladium exist only when large amounts of hydrogen have been occluded. The presence of sufficient hydrogen can easily be brought about by the addition of pure hydrogen made in the apparatus already described. (The procedure here is similar to the addition of oxy-hydrogen gas in the explosion analysis.) Yet even when the hydrogen is added, the reaction fails if the gas mixture to be analysed contains certain other substances, as it always does in technical analyses. We have there to deal with very complicated gas mixtures from which the other gases—carbon dioxide, heavy hydrocarbons, oxygen, carbon monoxide, etc.—must first be separated by absorption. The gases just mentioned may in a few minutes be separated by absorption with great ease and with a completeness more than sufficient for practical ends, so that less than tenths of a per cent of the gases remain in the gas

residue. It is, however, very difficult, and, in a short space of time, impossible to separate traces less than tenths per thousand, for the well-known reason that the rapidity of absorption diminishes with the dilution of the gas. And since, further, some of the absorbents give up gases—the solutions of cuprous chloride give off, according to whether they are acid or alkaline, either hydrochloric acid or ammonia—the residue which remains after the absorption of the absorbable gases consists of hydrogen, nitrogen, and marsh-gas and an undeterminable amount of carbon dioxide, heavy hydrocarbons, oxygen, and vapours of hydrochloric acid or ammonia. This gas residue deports itself differently from the mixture of pure hydrogen, nitrogen, and marsh-gas; with quite active palladium sponge coated with a very thin layer of oxide, no heating-up and no absorption take place.

Upon investigating the behaviour of different gases in the presence of hydrogen toward palladium which contains palladious oxide, it was found that hydrogen could be sharply separated by this reaction—

(1) from marsh-gas and nitrogen,
(2) from ethylene and nitrogen,
(3) from carbon dioxide and nitrogen;

that aqueous vapour and traces of ammonia do not interfere; but that carbon monoxide, large quantities of benzol vapour or alcohol vapour, and traces of hydrochloric acid do interfere.

The reason for this behaviour is that the affinity of the gases last named for the oxygen of the palladious oxide equals or exceeds that of hydrogen, so that they first burn at the expense of the palladious oxide,

and in so doing do not develop enough heat to make the occlusion of the hydrogen possible.

Since we have here to deal with a combustion which, as it happens, takes place at ordinary temperatures, the author believes it must be possible to separate the gases in question with the aid of other metallic oxides and other temperatures, if we could only succeed in raising the temperature slowly and exactly with the help of suitable thermostats, and in keeping the interior of the tube at the same temperature as that prevailing on the outside by diluting the metallic oxides with metals. In this way it might be possible, with the use of simple apparatus, to make the whole gas analysis by fractional combustion. We may call to mind in this connection that in badly performed elementary analyses tarry products distil over feebly-glowing copper oxide.

If oxygen is present with hydrogen in the palladium reaction, the oxygen is burned completely to water. But the combustion of the marsh-gas may also take place if the heat rises too much, *i.e.* at temperatures near that of red heat. This rise of temperature may be caused by improperly preparing the palladium in spherical masses, so that the heat evolved during the reaction is then only insufficiently set free by radiation. The difficulties which stand in the way of using palladium, because of the particulars just mentioned, are completely avoided if the absorbable gases are first removed as far as possible, if only an ammoniacal cuprous chloride solution is used, if for the combustion of the last traces of carbon monoxide, ammonia, etc., somewhat more palladium, 4 to 5 gr., is used, and if during the reaction itself the tube with

the palladium stands in water of from 90° to 100° temperature. Before using the palladium it is heated, in portions of about 1 grm. at a time, nearly to redness upon the cover of a platinum crucible, so that it is covered with a larger quantity of palladious oxide than would be formed by merely leading air over it. The warm water in which the tube stands serves in the beginning to give the gases the temperature necessary to start the combustion, and later it prevents the temperature inside the palladium tube being raised too high by the reaction.

Palladium-black is still more active than the palladium sponge which has been coated with palladious oxide by heating it to redness.

This palladium-black is made by reducing palladious chloride with alcohol in a strongly alkaline solution, the same method being used in preparing platinum-black from platinum chloride. Palladium-black, which is active even in the presence of vapours of hydrochloric acid, is either an oxygen compound of palladium or a mixture of metallic palladium with palladious oxide.

The arrangement of the apparatus for carrying out the reaction is shown in Fig. 55. The gas burette *A* and the gas pipette *B* are joined together by means of the capillary tubes *E* and the tube *H*. This tube *H* is of about 4 mm. internal diameter and 20 cm. total length, and it contains 4 grams of palladium sponge.

The gas pipette upon the stand *G* is filled with water, and its only use is to render it possible to repeatedly pass the gas through the palladium tube.

To determine the amount of hydrogen present in a mixture of hydrogen, nitrogen, and marsh-gas, from

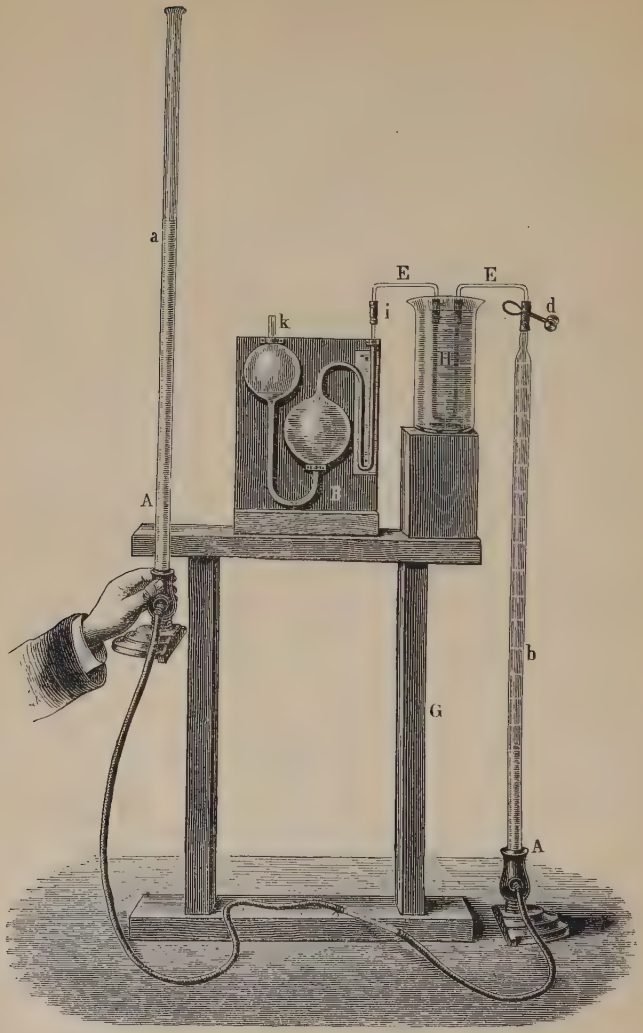

Fig. 55.

which, so far as possible, the absorbable constituents have already been removed, measure the gas in the burette, join it in the manner described to the pipette *B*, which is filled with water nearly to *i*, place the tube *H* in a large beaker containing warm water of from 90° to 100°, and, after opening the pinchcock *d*, drive the gas three times back and forth through the palladium by raising and lowering the tube *a*. Then replace the hot water with water of the temperature of the room, and lead the gas residue twice back and forth through the tube in order to completely cool the gas. It is in this manner possible to absorb with certainty every particle of hydrogen. Upon drawing the gas so far back into the measuring tube that the water in the pipette again stands near *i*, the difference between the two measurements made before and after the absorption corresponds to the hydrogen + the amount of oxygen in the air enclosed in the U-tube when the apparatus was put together. This air volume, and therewith its oxygen contents, may be determined with sufficient exactness once for all by closing, with a piece of rubber tubing and glass rod, one side of the tube filled with palladium, cooling the tube to about 9° C. by placing it in cool water, and then, after connecting it by a capillary with a gas burette completely filled with water, warming it to 100° by placing it in boiling water. The expansion of the enclosed air volume corresponds to a difference of temperature of 91°, *i.e.* to a third of the enclosed volume of gas.

The palladium is regenerated after the reaction by first leading air over it, whereby it becomes quite hot; removing any drops of moisture which may collect, so

that the palladium may easily be shaken out of the tube in the form of a dry powder; and then superficially oxidising the metal by heating it on the lid of a platinum crucible.

The residue of nitrogen and marsh-gas which remains after the absorption of the hydrogen is burnt by explosion in the manner to be later described.

With the aid of the apparatus here mentioned, the occlusion of hydrogen by palladium may be very strikingly shown; the burette is filled with pure hydrogen from the hydrogen pipette, and is then connected with

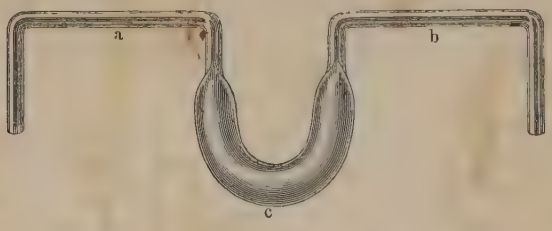

Fig. 56.

the pipette by means of a glass tube (Fig. 56) in which $2\frac{1}{2}$ grams of palladium sponge containing some palladious oxide are enclosed. *a* and *b* are capillary, and *c*, which contains the palladium, is about 5 mm. wide.

Upon leading the hydrogen through the tube, the absorption begins at once without the aid of external heat, and the palladium becomes quite hot; in a very short time, after the gas has been passed but a few times back and to through the palladium, all of the hydrogen disappears. If air is now drawn through the palladium by means of a bottle aspirator or any similar suction arrangement, the hydrogen burns, the

palladium being usually seen to glow at some points; the palladious oxide necessary for the reaction is thus formed, and the tube is ready for a repetition of the experiment.

The following analyses serve as illustrations of this method of absorption.

1. Analyses are here given of two mixtures of nitrogen and marsh-gas made at different times and by the usual method from sodium acetate, and freed by palladium from the hydrogen which is always simultaneously given off. The gases contained, before the absorption with palladium, 6·2 per cent of hydrogen. The analyses were made over mercury with the apparatus for exact gas analysis described in Part I., Chap. III., and they showed that it is actually possible to completely free marsh-gas by means of palladium from any hydrogen which it may contain.

The nitrogen of the mixture comes from the air which was not thoroughly driven out during the evolution of the gases, and in the present analysis is of no importance.

The combustion analysis gave the following results :—

I.	Marsh-gas calculated from the contraction .	52·45
	„ „ „ carbon dioxide	52·3
II.	Marsh-gas calculated from the contraction .	50·25
	„ „ „ carbon dioxide	50·1

The agreement of these figures is quite sufficient to show that the gases must be regarded as mixtures of marsh-gas and nitrogen free from any noticeable quantities of hydrogen.

2. Analyses here follow of artificial mixtures of

hydrogen, marsh-gas, and nitrogen, the marsh-gas being previously freed from any hydrogen it might contain by means of palladium.

(*a*) 27·2 ccm. marsh-gas and nitrogen mixed with 47·5 ccm. hydrogen gave, after absorption with palladium—

27·2 ccm.

(*b*) 27 ccm. marsh-gas and nitrogen mixed with 54·6 ccm. hydrogen gave, after absorption with palladium—

27 ccm.

(*c*) 13·3 ccm. marsh-gas and nitrogen mixed with 41·6 ccm. hydrogen gave, after absorption with palladium—

13·3 ccm.

3. Four analyses of Dresden illuminating gas gave 50·7, 50·6, 50·6, 50·6 per cent hydrogen. The mean of several explosion analyses was 50·5 per cent.

As an example for the calculation, the following analysis of Dresden illuminating gas (April 2d, 1879) is given. The direct absorptions gave—

3·5	per cent	carbon dioxide
4·2	„	heavy hydrocarbons
0·2	„	oxygen
10·6	„	carbon monoxide.

The reading after absorption with palladium gave a decrease of volume of 51·5 ccm.

The air contained in the palladium tube was 1·9 ccm., hence the oxygen therein amounted to 0·4 ccm.

Since this oxygen was burned during the reaction,

the volume of hydrogen sought is $51{\cdot}5 - 0{\cdot}4 = 51{\cdot}1$ per cent. Of the gas residue of marsh-gas and nitrogen remaining after the hydrogen had been absorbed, 15 ccm. were measured off in a burette and the remainder was kept in reserve in a pipette.

To the 15 ccm. of gas the desired quantity of air was added by lowering the level-tube and opening the pinchcock. The air here added was 82·6 ccm. The mixture was transferred to the explosion pipette, and then as much more air was measured off in the pipette as was probably necessary for the complete combustion of the gas residue, and this air was also brought into the explosion pipette.

For the 15 ccm. of gas residue of marsh-gas and nitrogen 160 ccm. of air were added; in other words, the second portion added amounted to 77·4 ccm.

The gases were thoroughly mixed in the pipette by vigorous shaking, and were then exploded. After the explosion, the gas was led into the caustic potash pipette to absorb the carbon dioxide formed, and was then measured.

The residue was more than the burette could hold, and on this account it was measured in two portions. Results :—

First portion	97·5
Second portion	38·0
Total volume after explosion	135·5

Hence the contraction was—

$$160 \text{ ccm.} + 15 \text{ ccm.} - 135{\cdot}5 \text{ ccm.} = 39{\cdot}5 \text{ ccm.},$$

which corresponds to 13·2 ccm. marsh-gas.

Since the contents of the palladium tube was 1·9

ccm., and the volume of the total residue of marsh-gas and nitrogen 30·4 ccm., the total amount of marsh-gas is given by the proportion—

$$15 : 30{\cdot}4 + 1{\cdot}9 = 13{\cdot}2 : x.$$
$$x = 28{\cdot}42 \text{ per cent marsh-gas.}$$

The nitrogen is found by subtracting the sum of all the constituents from 100. The result in this case is 2. Hence the composition of the gas is as follows :—

3·5	per cent	carbon dioxide
4·2	„	heavy hydrocarbons
0·2	„	oxygen
10·6	„	carbon monoxide
51·1	„	hydrogen
28·4	„	marsh-gas
2·0	„	nitrogen.

The Absorption of Hydrogen by Potassium and Sodium.

Jacquelain[1] has made use of the property of potassium of absorbing hydrogen as a means of separating hydrogen, marsh-gas, and ethylene.

Potassium and sodium can be melted in an atmosphere of hydrogen without absorbing the gas. The absorption begins at 200° and attains its maximum between 300° and 400°: potassium hydride and sodium hydride, substances similar to silver amalgam, are formed. These compounds can be melted in vacuum without decomposition. Heated in vacuum to above 200° they give up hydrogen. At 430° the decomposition in vacuum is complete.

Potassium absorbs, according to Troost and Haute-

[1] *Ann. Chim. Phys.* **74**, 203.

feuille, 124·6 volumes of hydrogen; sodium, on the other hand, 23·8 volumes. At 421° the absorption ceases, unless the hydrogen is led in under pressure.

These hydrogen compounds are decomposed by mercury, with formation of potassium or sodium amalgam. These amalgams have no longer the property of absorbing hydrogen.

The author has repeatedly endeavoured to work out a convenient method for making this absorption.

Mercury forms with sodium a solid amalgam, and at the same time sets free again any hydrogen with which the sodium may have united, while petroleum begins to decompose at 400°. Hence we have no confining liquid which may be used to drive the gas completely from one piece of apparatus to another.

The author has sought to use, in a double gas pipette, the alloy of potassium and sodium which is fluid at ordinary temperatures, as confining liquid, but he has finally come to the conviction that this method cannot be employed because of the fact that the slightest trace of oxygen or moisture causes a stoppage of the capillary by the formation of potassium or sodium oxide.

Sodium may conveniently be used for determining hydrogen if the gases are drawn from one vessel to another by means of a small Töpler air-pump of the form used by the author [1] for elementary analysis.

Nitrous Oxide (N_2O).

Specific gravity, 1·52269. Weight of 1 litre, 1·97023.

[1] Fresenius, *Zeitschrift für analytische Chemie*, **17**, 409.

According to Carius, nitrous oxide is quite soluble in water. One volume of water dissolves, at 760 mm. pressure and 20°, 0·670 volumes.

The coefficient of absorption is—

$$1{\cdot}30521 - 0{\cdot}045362t + 0{\cdot}0006843t^2.$$

For alcohol it is—

$$4{\cdot}17805 - 0{\cdot}069816t + 0{\cdot}000609t^2,$$

and 1 volume of alcohol takes up at 20° 3·0253 vol. N_2O.

Bunsen determines nitrous oxide by combustion with hydrogen and oxyhydrogen gas, the nitrous oxide being thereby split up into water and nitrogen. Since this is a purely volumetric method, it follows that quantities of nitrous oxide which are less than about a fifth of a per cent of a gas mixture cannot be thus determined.

The idea is advanced in different places in the literature of the subject that this method is not exact because of accompanying reactions.

The author has examined the method,[1] and has found that the results are quite satisfactory if the volume of hydrogen is two to three times that of the nitrous oxide, and if such an amount of oxyhydrogen gas is added that to 100 volumes of incombustible gas there will be between 26 and 64 volumes of combustible gas. The combustion is made in the explosion pipette. The decrease of volume is equal to the volume of the nitrous oxide.

Two volumes of nitrous oxide are made up of 2 volumes of nitrogen and 1 volume of oxygen, and

[1] *Berichte der deutsch. chemischen Gesellschaft*, 1882, p. 903.

require for combustion 2 volumes of hydrogen. After the combustion, the hydrogen and oxygen have disappeared, but the nitrogen has been set free, hence the contraction is equal to the volume of nitrous oxide sought. Cl. Winkler has proposed[1] to determine nitrous oxide by leading it through a capillary in which a palladium wire is electrically heated to redness; the volume of the gas is thus increased one half:—

$$2N_2O = 2N_2 + O_2,$$
$$2 \text{ vol.} = 2 \text{ vol.} + 1 \text{ vol.}$$

This method is, however, not so sharp as the preceding, because the change of volume here amounts to only one half of the volume of the nitrous oxide, while in the combustion this change is as large as the volume of the N_2O. Special chemical absorbents for nitrous oxide are not known.

On account of the great solubility of nitrous oxide, contact between the gases to be analysed and aqueous solutions must be avoided as far as possible.

At the present time no method exists for detecting traces of nitrous oxide.

Nitric Oxide (NO).

Specific gravity, 1·03764. Weight of one litre, 1·34261.

The coefficient of absorption for temperatures between 0° and 25° is, according to Carius, for alcohol—

$$0{\cdot}31606 - 0{\cdot}003487t + 0{\cdot}00004t^2.$$

[1] *Anleitung zur chem. Untersuchung der Industrie-Gase*, Part II p. 427.

Nitric oxide cannot be determined by combustion with hydrogen because, as shown by the researches of Bunsen, the combustion is not a complete one; even when the explosion is quite violent, incomplete combustion to nitrous oxide takes place.

Nitric oxide is determined by absorption with solutions of ferrous salts, which are used in a double pipette. One part of ferrous sulphate is dissolved in two parts of water. The analytical absorbing power is 3.

Solutions of potassium hydroxide and sodium hydroxide do not absorb nitric oxide.

The nitric oxide present in a current of gas may be determined by leading the gas through a solution of potassium permanganate acidified with sulphuric acid. The following reaction takes place :—

$$10NO + 6KMnO_4 + 9H_2SO_4 = 3K_2SO_4 + 6MnSO_4 + 10HNO_3 + 4H_2O.$$

Nitrogen Trioxide (N_2O_3).

The best absorbent for nitrogen trioxide is concentrated sulphuric acid of at least 1·702 sp. gr.

Nitrogen trioxide is easily absorbed by alkaline solutions with formation of nitrites.

Potassium permanganate absorbs the gas and oxidises it to nitric acid. In the presence of sulphuric acid the reaction is—

$$5N_2O_3 + 4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 10HNO_3 + H_2O.$$

Nitrogen Tetroxide (NO_2).

This gas is actively absorbed by alkaline solutions

and by sulphuric acid. By potassium permanganate it is changed to nitric acid.

$$10NO_2 + 2KMnO_4 + 3H_2SO_4 + 2H_2O = K_2SO_4 + 2MnSO_4 + 10HNO_3.$$

Ammonia (NH_3).

Specific gravity, 0·5889. Weight of one litre, 0·76199. One volume of water absorbs, according to Bunsen—

At 700 mm. and 0° . . .	1114
„ „ 20° . . .	645·2
At 800 mm. and 0° . . .	1128
„ „ 20° . . .	701·7.

Alcohol and ether also absorb considerable quantities of the gas.

Measured quantities of dilute hydrochloric or sulphuric acid are used to absorb the gas, and the amount of ammonia is determined by titrating back with a standard solution of an alkali.

If a direct determination is not possible, as, for instance, in gases containing large amounts of tar, the ammonia may be absorbed in sulphuric acid, and the nitrogen present may then be set free and measured in a Knop azotometer.

This simple and very exact method has been further worked out by Wolf, Dietrich, P. Wagner, and F. Soxhlet.[1] It is based upon the action of alkaline hypobromites upon salts of ammonia, all nitrogen present being set free.

$$3NaBrO + 2NH_3 = N_2 + 3H_2O + 3NaBr.$$

If urea is present, its nitrogen is also set free.

[1] Fresenius, *Quantitative Analyse*, 6th ed., Part II., pp. 681 and 715.

The apparatus is shown in Fig. 57; the description of the method is taken from Fresenius.

The bottle *a*, in which the solution of sodium hypobromite is allowed to act upon the ammonium

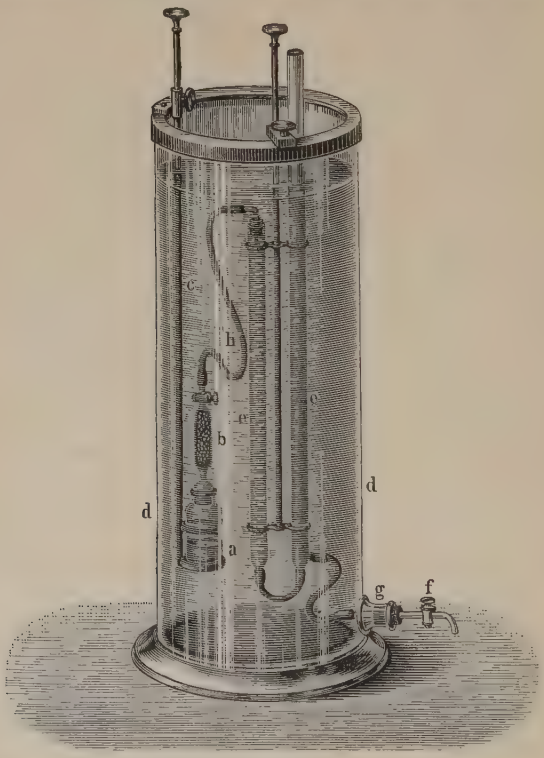

Fig. 57.

salts, is from 10 to 11 cm. high, of 51 mm. diameter, and is closed by a hollow glass stopper, to which is fused a thick glass tube *b*, 8 to 9 cm. long and 2 cm. in diameter. This can be closed at the top by a glass

stopcock, to the other side of which a thick-walled, tapering glass tube is attached. The wide tube is closely filled with large glass beads, and is closed at the lower end with a loose ball of fine platinum wire, so that the beads cannot fall into *a*. The iron rod *c* has at its lower end a metal plate, and, a little above, a clamp for carrying the bottle *a*; by means of the rod the bottle can be immersed in the water in the glass cylinder *d*, which is 50 cm. high and 18 cm. wide. The rod can be moved up and down through a collar, and may be fastened in any position by means of a screw. The upper edge of the glass cylinder *d* is covered with a brass band. Two short steel pins, projecting upward from this band, pass through openings in the collar attachment of the rod *c*. The rod can thus be easily detached or set on again.

To the brass ring is also attached the metal holder of the U-tube *e*, one arm of which is graduated. The holder is held in place by a screw. Upon loosening this screw and detaching the stopcock *f* from the rubber tube by taking *f*, with its stopper, out of the opening *g*, the whole U-tube may be taken out when it is necessary either to clean it or to renew the rubber tubes. By means of the stopcock *f* and its rubber tube, water can be let out of the plain arm of the U-tube *e*. This arm of the U-tube is somewhat longer than the graduated arm, and it must project some centimetres above the level of the water in *d*, so that the U-tube may be filled with distilled water. The lower ends of the arms of the U-tube are joined together by a rubber tube. To connect the lower end of the plain arm with the stopcock *f*, a piece of rubber

tubing about 20 cm. long is slipped over the short side arm of *e*; the U-tube is then lowered into the cylinder, and the rubber tube is drawn through *g* by means of a little hook. The tube of the stopcock is inserted through the stopper, the rubber tube is then slipped over the projecting end of the tube, and the stopper is pushed firmly into *g*. If an ordinary cork is used, it is advisable to dip it into molten paraffin after boring the hole through it.

The rubber tube *h* which connects the graduated arm of the U-tube with *b* and *a* has an internal diameter about as large as a knitting-needle; it must be thick-walled and of soft rubber. Its length is such that *a* may be taken out of the water and be placed on the table without subjecting the rubber tube to any tension. With such a length, no change in the volume of the rubber tube need be feared, and the shaking and inverting of *a* outside of the cylinder *dd* can be conveniently performed.

In using the apparatus for analyses, the amount of nitrogen actually given off in the apparatus is determined by using a normal ammonium chloride solution; in the second experiment, the liquid in question is put into *a*. The difference between the found and calculated amount of nitrogen in the first experiment gives a correction, which is introduced in the calculation of the results from unknown amounts.

Methyl-Amine ($NH_2.CH_3$).

Specific gravity, 1·13.

1 volume of water absorbs at 12° 1040 volumes.
1 „ „ „ 25° 955 „

It condenses at a temperature somewhat under 0°. It is absorbed by acids.

Carbon Dioxide (CO_2).

Specific gravity, 1·51968. Weight of one litre, 1·96633.

According to Bunsen and Pauli, one volume of water takes up

$$1{\cdot}7967 - 0{\cdot}07761t + 0{\cdot}0016424t^2.$$

To absorb carbon dioxide either potassium hydroxide or barium hydroxide is used.

For volumetric determinations, a solution of 1 part of commercial caustic potash in 2 parts of water is employed. Analytical absorbing power, 40 ccm. carbon dioxide. This solution is put into the simple pipette for solid and liquid reagents (Fig. 21), the cylindrical part b_1 being first closely filled with very short rolls of iron wire-gauze. The gauze has a mesh of 1 to 2 mm., and the rolls are from 1 to 2 cm. long and about 5 mm. thick.

When the per cent of carbon dioxide is not too high, it can be completely absorbed by simply passing the gas once into the pipette. The complete manipulation does not take one minute.

Since a $33\frac{1}{3}$ per cent solution of caustic potash is quite viscous, so much of the reagent remains hanging on the gauze when the gas is introduced, that on the one hand the absorption of the carbon dioxide takes place at once, and on the other hand the simultaneous absorption of oxygen, caused by the oxidation of the

iron, is impossible, because the gauze is completely protected by the solution from the action of the air, as repeated experiments have shown.

The wire-gauze has a further advantage. It cools the warmed gases at once down to the temperature of the room, so that the absorption of the carbon dioxide formed in the combustion of marsh-gas (see later) may also be very suitably made in the carbon dioxide pipette.

Small quantities of carbon dioxide are best determined by absorption in a solution of barium hydroxide and titration with oxalic acid.

Carbon Monoxide (CO).

Specific gravity, 0·96709. Weight of one litre, 1·25133. One vol. water dissolves, according to Bunsen,

$0{\cdot}032874 - 0{\cdot}00081632t + 0{\cdot}000016421t^2$ volumes of carbon monoxide; hence

At 20°, 0·02312.

According to Carius, alcohol dissolves between 0° and 25°, 0·20443 vol. CO.

For absorbing carbon monoxide either an ammoniacal or a hydrochloric acid solution of cuprous chloride is used.

The ammoniacal solution of cuprous chloride is prepared (the amounts here given make 200 ccm.) by dissolving 10·3 grams of copper oxide in 100 to 200 ccm. of concentrated common hydrochloric acid, and then allowing the solution to stand in a flask of suitable size, filled as full as possible with copper

wire or copper wire-gauze, until the cupric chloride is reduced to cuprous chloride, and the solution is completely colourless. The clear hydrochloric acid solution thus prepared is poured into a large beaker glass or cylinder containing $1\frac{1}{2}$ to 2 litres of water, to precipitate the cuprous chloride formed. After the precipitate has settled, the dilute hydrochloric acid is poured off as completely as possible, the cuprous chloride is then washed into a 250 ccm. flask with about 100 to 150 ccm. of distilled water, and ammonia is led into the solution, which is still slightly acid, until the liquid takes on a pale blue colour. Since the tension of very concentrated ammonia solutions renders the absorption difficult, no more ammonia than is necessary should be added. While the ammonia is being led in, it is well to protect the contents of the flask from the oxidising influence of the air. This may be done by fitting the flask containing the cuprous chloride to be dissolved, with a double-bored stopper through one opening of which passes the delivery tube from the ammonia flask, while through the other opening is inserted a bent glass tube which dips into a little mercury. If a flask with a funnel-tube is used for the evolution of ammonia, hydrogen may first be led through this tube, and the apparatus be thus completely freed from air. For the evolution of ammonia, about 200 ccm. of a concentrated ammonia solution of 0·9 sp. gr. is used.

The solution of cuprous chloride thus prepared is diluted with water to 200 ccm., and, since the hydrochloric acid was not entirely washed out, there is of course some ammonium chloride present. 100 ccm. contain 7·3 grams of cuprous chloride.

The analytical absorbing power of this solution is 6 ccm. of carbon monoxide.

It is quite impracticable to use more dilute solutions of cuprous chloride.

For the preparation of the hydrochloric acid solution of the cuprous chloride, Winkler directs that 86 grams of copper scale be mixed with 17 grams of copper powder, prepared by reducing copper oxide with hydrogen, and that this mixture be brought slowly, and with shaking, into 1086 grams of hydrochloric acid of 1·124 sp. gr. A spiral of copper wire reaching from the bottom to the neck of the bottle is then placed in the solution, and the bottle is closed with a soft rubber stopper. The solution is dark at the beginning, but it becomes completely colourless on standing; in contact with the air it takes on a dark brown colour, due to the formation of some cupric chloride.

The analytical absorbing power is 4 ccm. of carbon monoxide.

If, after the absorption of the carbon monoxide in a gas mixture, the hydrogen is to be determined with palladium, the ammoniacal solution must be used. If the amount of carbon monoxide alone is to be ascertained, the hydrochloric acid solution may be employed with equally good results. These solutions of cuprous chloride are used in the double pipette (Fig. 22).

H. Drehschmidt[1] has shown, however, that the union of carbon monoxide with cuprous chloride is so feeble that upon shaking a solution which has taken up any considerable quantity of carbon monoxide, this gas is again given up in an atmosphere free from

[1] *Berichte der deutsch. chemischen Gesellschaft*, **20**, 2344; **20**, 2752; and **21**, 2158.

carbon monoxide. For this reason two pipettes are used in the absorption, one pipette containing a frequently used, the other a but slightly used, solution of cuprous chloride. In the absorption, the gas in question is first shaken for two minutes with the first-mentioned solution, and is then transferred to the second pipette containing the but slightly used solution, and is shaken three minutes therein. According to Drehschmidt, the ammoniacal solution is to be preferred to the hydrochloric acid one.

Solutions of cuprous chloride have no considerable tension, so that this may be disregarded in analyses which are to give only approximate results, or in which no great accuracy is necessary. In exact determinations, however, the gases which have been in contact with the reagent must be freed from the gaseous hydrochloric acid or from the ammonia; this can be brought about in the burette itself, or in a pipette filled with distilled water.

The solutions of cuprous chloride are thin, and they flow readily; hence it is unadvisable to make the absorption in the double pipette for solid and liquid reagents (Fig. 23), in which the cylinder *a* has been filled with copper wire-gauze, for the absorption is not here effected, as with carbon dioxide, by simply leading the gas once into the pipette; on the contrary, it can be brought about only after some time by frequently repeating this operation.

The solutions of cuprous chloride are absorbents not only for carbon monoxide and acetylene, but also for ethylene—a fact which is not taken into account in a number of gas analyses lately published, and the disregard of which must of course lead to wholly useless results.

The author was unable to find any notice of this particular in the existing literature, and by the recurrence of an error in an analysis of illuminating gas he was led to investigate the behaviour of cuprous chloride toward ethylene. He at first believed that marsh-gas was somewhat soluble in cuprous chloride, but further experiments showed that this was not the case.

To study the action of ethylene toward cuprous chloride, 25 parts by weight of absolute alcohol were mixed with 150 parts by weight of concentrated sulphuric acid, and the gas given off upon careful heating was passed, first through an empty bottle and then through concentrated sulphuric acid and through several wash-bottles filled with a concentrated solution of potassium hydroxide. After the evolution of gas had gone on for an hour, the gas was collected in a small glass gasometer over a strongly alkaline solution of pyrogallic acid, and was analysed after standing for several days. 91·3 per cent of the gas was absorbable by concentrated sulphuric acid.

Another portion of the gas, brought together with a hydrochloric acid solution of cuprous chloride, gave 94·3 per cent of absorbable gas.

Another sample of ethylene prepared by the same method gave, in two experiments with hydrochloric acid cuprous chloride, 94·5 per cent of absorbable constituents.

In two experiments with ammoniacal cuprous chloride, 95·0 per cent of absorbable constituents.

These last four analyses were not made in pipettes, but in the simple gas burette with unsaturated reagent. The difference in the results is caused by the different solubility of nitrogen in ammoniacal and hydrochloric

acid cuprous chloride, and it is as large as it is because the residual 5 ccm. of gas in the analysis came into intimate contact with 95 ccm. of unsaturated absorbing liquid.

In the method of preparing ethylene described above, some carbon is always separated, and this, upon being heated with sulphuric acid, gives off carbon monoxide in addition to sulphur dioxide and carbon dioxide. The presence of the carbon monoxide completely explains why the cuprous chloride absorbed 3 per cent more gas than the fuming sulphuric acid.

Certain analytical data indicate that the heavy hydrocarbons are not equally absorbable by the reagent. Ethylene appears to be absorbed with especial ease. It remains, therefore, to ascertain whether cuprous chloride itself cannot be used for separating the heavy hydrocarbons.

Preliminary experiments showed further, that the gases not absorbable by cuprous chloride are much more soluble in this reagent than in other absorbing liquids. This fact shows that, to obtain accurate results, a cuprous chloride solution which has been saturated with the gases but slightly soluble in it must unquestionably be used.

In the three determinations, given later, of carbon monoxide in an illuminating gas from which the carbon dioxide, heavy hydrocarbons, and oxygen had been absorbed, 8·6 and 8·5 per cent of carbon monoxide was found with unsaturated reagent, and 8·1 per cent with reagent which had been saturated by repeated use, but which still possessed high absorbing power.

These experiments showed further that the cuprous chloride solution is not suited to the absorption of

oxygen, since complete absorption is attained only after shaking for a very long time. The gases to be treated with this reagent must on this account be free from oxygen.

The author has also found that the hydrochloric acid solution of cuprous chloride is not changed by petroleum, so that this reagent may be kept under petroleum in a bottle having at the bottom a tubulus and stopcock; the bottle should be completely filled and tightly stoppered. If, after some cuprous chloride has been taken out, the bottle is kept full of petroleum and tightly closed, the solution does not change in strength.

In May, 1885, Mr. Karl Markel, chemist of the Ammonia-soda Works at Winnington, England, called the author's attention to the fact that in the absorption of carbon monoxide with cuprous chloride, the gas volume at times did not decrease, but on the contrary became considerably greater. He sent a number of analyses of generator gases in confirmation of his statement. In none of these analyses were the heavy hydrocarbons determined either by fuming sulphuric acid or any other reagent, so that it was surmised that these gases might be the cause of the irregularity. Experiments have borne out this assumption, and have shown that even when the determination of the heavy hydrocarbons is of no importance for the analysis, they must nevertheless be removed before the carbon monoxide is absorbed with cuprous chloride.

If ethylene is absorbed with cuprous chloride, and this solution is then used for the absorption of carbon monoxide, a certain quantity of ethylene is set free, so that the results of the analysis are of course erroneous.

If the same solution of cuprous chloride is used for a large number of absorptions, the case may arise that the gas volume does not decrease when the carbon monoxide is absorbed, but on the contrary is increased by the ethylene set free. It is obvious that an increase of volume may also be caused by carbon monoxide being set free in the manner mentioned by Drehschmidt.

Cl. Winkler[1] has found that if palladious chloride be added to solutions of cuprous chloride in hydrochloric acid, ammonium chloride, or sodium chloride, then these solutions, if they have absorbed carbon monoxide, give upon dilution with water a precipitate of metallic palladium, the carbon monoxide being at the same time oxidised to carbon dioxide.

F. P. Treadwell and H. N. Stokes[2] have shown that carbon monoxide can be completely absorbed with fuming nitric acid, if the two are shaken together for quite a long time (25 minutes).

Small quantities of carbon monoxide may be detected by means of blood. H. W. Vogel[3] was the first to use the well-known spectrum reaction of blood impregnated with carbon monoxide, as a means of finding small amounts of the gas. This reaction is of especial significance, because the carbon monoxide cannot be confounded with another gas—a fact which, on account of the highly poisonous character of the substance, is of great importance in analyses undertaken from a sanitary standpoint.

To detect carbon monoxide, Vogel directs that a

[1] Fresenius, *Zeitschrift für analyt. Chemie*, **28**, p. 269.
[2] *Berichte der deutsch. chemischen Gesellschaft*, 1888, p. 3131.
[3] *Ibid.* **11**, 235. Also **10**, 792.

100 ccm. bottle, filled with water, be emptied in the room containing the gas, and that 2 to 3 ccm. of blood, highly diluted with water, and showing only a very faint red colour, yet still giving the well-known absorption bands in a column as thick as a test-tube, be poured into the bottle and shaken for some minutes. When carbon monoxide is present, the blood at once takes on a rose colour, and upon the addition of a few drops of strong ammonium sulphide the absorption bands do not disappear. In blood free from carbon monoxide the absorption bands are in this reaction replaced by a broad and weakly defined band.

Vogel states that amounts down to 0·25 per cent

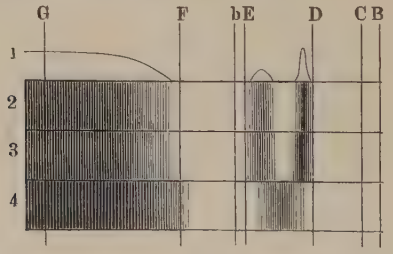

Fig. 58.

can be clearly detected, but that the delicacy is not increased by using greater volumes of air.

The author found by experiment that it was not possible, in a Liebig potash-bulb or by shaking, to completely remove very small amounts of carbon monoxide from a gas mixture by means of an exceedingly dilute solution of blood, such as Vogel employs; and he also found that concentrated solutions of blood could not be used because they foam so much. He was thus led to the idea that by using living animals, whose lungs

would furnish an absorption apparatus of incomparable completeness and admit of the use of undiluted blood, it might be possible to still further increase the delicacy of the reaction.

This supposition was proved correct by the experiments which follow, and it led to a more delicate method for detecting carbon monoxide.

Mice were used in the work, and they were exposed to the action of the gas to be tested for carbon monoxide by placing them between two funnels joined together at the mouths by means of a broad band of thin rubber. The ends of the funnels were connected to the gasometers and absorption apparatus by pieces of rubber tubing.

To bring the mouse, without hurting it, into this simple apparatus, the animal is first dropped into a large and wide glass cylinder. It is then covered with one of the funnels, a glass plate is slipped under the funnel, and the mouse is lifted out. The mouth of the second funnel is then brought opposite that of the first one, the glass plate is drawn out, and the funnels are joined together by the rubber band.

Mixtures of air and carbon monoxide were used in the experiments. The carbon monoxide was made with great care, either from potassium ferrocyanide and sulphuric acid, or from oxalic acid and sulphuric acid, and was washed with a sodium hydroxide solution. The lighter carbon monoxide was led into the air from below, and the mixture was allowed to stand and diffuse for at least twelve hours.

The current of gas was so regulated that ten litres of gas passed through the apparatus in from one to two hours, and the gases coming from the funnels con-

tained from 0·3 to 2·8 per cent of carbon dioxide, resulting from the respiration of the mouse. Frequently repeated analyses showed, however, that this carbon dioxide did not usually rise above 1 per cent, so that it was impossible for it to cause any seriously injurious results.

In some experiments also, as is described in detail below, a Liebig potash-bulb filled with a fresh blood solution, which was highly diluted according to Vogel's directions, was placed either before or after the animal.

The mice were killed by immersing the funnels in water, and a considerable quantity of blood was obtained by cutting them in two in the region of the heart.

The detection of the carbon monoxide hæmoglobin was always carried out with a freshly prepared solution of colourless ammonium sulphide; and to control the results, fresh blood of the same dilution and free from carbon monoxide was treated with the same amount of ammonium sulphide. To obtain this fresh blood a mouse which had not been in contact with carbon monoxide was killed shortly before the experiment.

To still further control the results, the author also used in most of the experiments freshly prepared ammonium ferrous tartrate, with the same success as with the ammonium sulphide. But the preference must be given to the colourless ammonium sulphide, because, when that is used, a difference in the colours of the reduced solutions when traces of carbon monoxide are present, is quite easily distinguishable even without the aid of the spectroscope. The liquid containing the carbon monoxide hæmoglobin is more distinctly red in colour.

A Vogel "universal spectroscope," made by Schmidt and Haensch, was used for observing the spectra.

Experiment 1.—The gas contained 0·022 per cent carbon monoxide. Before the animal there was placed an absorption apparatus containing blood. The mouse showed no symptoms of poisoning. Experiment was stopped at the end of three hours.

Carbon monoxide could be detected neither in the mouse nor in the interposed blood.

Experiment 2.—Gas contained 0·032 per cent of carbon monoxide. No absorption apparatus containing blood was placed before the animal.

The mouse showed no symptoms of poisoning. Experiment was stopped at the end of three hours.

The blood of the mouse gave a weak but unmistakable reaction for carbon monoxide.

Experiment 3.—Gas contained 0·032 per cent of carbon monoxide. Only an absorption apparatus containing a dilute blood solution was used.

Carbon monoxide could not be detected. Considerable albumen was coagulated, so that the solution, which previously had been clear, was now turbid.

Experiment 4.—Gas contained 0·043 per cent of carbon monoxide. The mouse showed no symptoms of poisoning. Experiment was stopped at the end of four hours. Distinct reaction for carbon monoxide. Even without the aid of the spectroscope, the presence of carbon monoxide could be clearly recognised from the red tone of the reduced blood.

Experiment 5.—Gas contained 0·067 per cent carbon monoxide. An absorption apparatus containing blood was interposed before the animal.

After half an hour slight symptoms of poisoning—

difficult respiration—could be seen. After three hours the experiment was stopped.

In the mouse the carbon monoxide could be plainly detected; the blood solution also gave the reaction, but much more faintly.

Experiment 6.—Gas contained 0·0593 per cent of carbon monoxide. An absorption apparatus containing blood was placed after the mouse.

After half an hour unmistakable symptoms of poisoning showed themselves—the mouse breathed with difficulty and lay exhausted on its side. The experiment was stopped at the end of $47\frac{1}{2}$ minutes. Carbon monoxide in the animal could be clearly recognised, but less plainly in the blood solution.

Experiment 7.—Gas contained 0·127 per cent of carbon monoxide. An absorption apparatus containing blood was placed before the animal.

At the end of only seven minutes there were strong symptoms of poisoning. The interposed blood solution, as well as the blood of the mouse, gave the reaction for carbon monoxide at the end of two hours.

Experiment 8.—Gas contained 2·9 per cent of carbon monoxide. In from one to two minutes the mouse died with convulsions. The blood gave a strong carbon monoxide reaction.

This last experiment shows vividly the frightfully poisonous action of carbon monoxide, for a few cubic centimetres of the still very dilute carbon monoxide suffice to produce at once strong symptoms of poisoning in a mouse.

Taking the results as a whole, we see—

(1) That when large volumes of gas (at the least 10 litres) are used, amounts of carbon monoxide down

to 0·05 per cent can be easily and certainly detected either by using dilute blood or a living animal (a mouse).

(2) That the limit of the test lies at about 0·03 per cent when a mouse is used, and with dilute blood at about 0·05 per cent.

(3) That decided symptoms of poisoning are observed from 0·05 per cent upwards.

The author is accordingly of the opinion that, to examine the air of a room for carbon monoxide, either the Vogel test must be used, a few cubic centimetres of very dilute blood being placed in an absorption apparatus and ten litres of air, at the least, being led through it, or, as is more convenient in many cases and also more delicate, that a mouse placed in an ordinary wire trap be allowed to breathe the air of the room for some hours, and the blood of the animal be then examined.

Vogel,[1] and, later, Gustav Wolffhügel, in his very interesting article upon "carbon monoxide and cast-iron stoves," [2] state that in their opinions quantities of carbon monoxide smaller than 0·25 per cent—the limit of the delicacy of the Vogel test when 100 ccm. of air is used—may be disregarded from a hygienic standpoint, and they would regard the presence of traces of carbon monoxide in the air of a room in the same light as one looks upon the presence of organic substances, of nitric acid, etc. in drinking water, or of carbon dioxide in the atmosphere. But, in the opinion of the author, this view cannot be accepted when we take into consideration the foregoing experiments, and

[1] *Berichte der deutsch. chemischen Gesellschaft*, **11**, 236.
[2] *Zeitschrift für Biologie*, **14**, 506.

the fact also that carbon monoxide does not belong, as does carbon dioxide, to the unavoidable constituents of the air of a room. Moreover, in inspecting heating arrangements the presence of any carbon monoxide should, from a sanitary standpoint, be regarded as inadmissible, this judgment being wholly independent of the statement

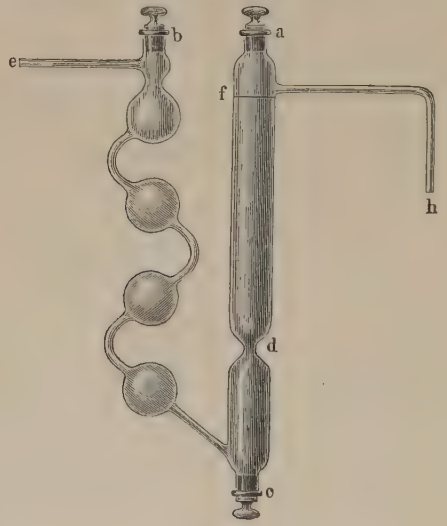

Fig. 59.

that there must be a lower limit at which carbon monoxide has no poisonous action on the human organism.

C. H. Wolff[1] has constructed a very effective absorption apparatus adapted to the use of small amounts of blood. He describes it as follows:—

"It corresponds essentially to the de Koninck modification of Mitscherlich's absorption apparatus, the difference being that at *a*, *b*, and *c* (Fig. 59) the tubes

[1] *Correspondenzblatt des Vereins analytischer Chemiker*, 1880, **3**, 46.

are closed by ground-glass stoppers, and that the cylinder is narrowed at *d*. In filling the apparatus, a little wad of glass-wool is inserted into *d* from above, and gently pressed into place, and the remainder of the tube as far as *f* is then filled with moderately fine powdered glass. This powdered glass is about as fine as ordinary gunpowder. It is freed from any fine powder and dust by sifting, and is then digested with hydrochloric acid, and carefully washed and dried. The great extent to which the size of these grains adds to the power of absorption through increase of surface is shown by the interesting researches of Dr. Soyka in Prague, upon the influences of the soil upon the decomposition of organic substances and the formation of nitric acid. The glass powder is moistened with water from above; strong suction is then applied at *e* by attaching an aspirator thereto, and the excess of water which is thus drawn off from the powdered glass is removed at *c*. Two cubic centimetres of dilute blood (1 : 40) is then allowed to drop from above, from a pipette, upon the moistened glass, *a* is closed, and by gently blowing into *h* with the mouth a uniform distribution of the blood solution throughout the column of powdered glass down to the glass-wool is effected. The apparatus is ready for the absorption, and it is now connected either at *e* with the aspirator or at *h* with the bottle, depending upon whether the 10 litres of air are to be drawn through or driven through. An ordinary bottle containing somewhat more than 10 litres is very well suited to the taking of the sample of the air to be examined. This bottle is supplied with a double-bore rubber stopper, through the openings of which pass two glass tubes bent at right angles

above the stopper. One of these tubes ends just below the stopper, and the other reaches to the bottom of the bottle. Pieces of rubber tubing of sufficient length, and closed by Bunsen screw-pinchcocks, are slipped over the free ends of both tubes. Since the bottle holds more than 10 litres, it is provided near the bottom with a mark, from which point up to the stopper the capacity is exactly 10 litres. To fill the bottle with the air to be examined, it is filled completely with water, and this is then run out through the rubber tube which is connected to the longer glass tube, and which acts as a siphon. When the water has fallen to the 10-litre mark both pinchcocks are closed. To pass the air through the absorption apparatus, the same rubber tube which has acted as a siphon is attached to a bottle filled with water, and standing higher than the first bottle, and the other rubber tube is connected with the absorption apparatus. The current of air, which may be very exactly regulated by means of the screw-pinchcock, must pass through the absorption apparatus very slowly—on an average, 1000 ccm. in twenty to twenty-five minutes. To be able to observe and regulate the passage of the air through the apparatus, 2 to 3 ccm. of water are run in at *b* after the powdered glass has been moistened with the blood solution. When the experiment is ended, this water is let out at *c*. Any burette holder is suited to holding the absorption apparatus; a Vogel 'universal stand' is also well adapted to the purpose. If it be desired to draw the air of the room in question directly through the apparatus,—a proceeding which is, however, not to be recommended because of the possible change in the composition of the air during

the long duration of the experiment,—the end *h* is joined by a cork to a so-called calcium chloride cylinder containing pieces of pumice-stone moistened with water. The air enters the cylinder from below, becomes saturated with moisture, and then passes into the absorption apparatus. When 10 litres of air have been led through, in one manner or the other, the stopper at *c* is removed to let out the water. A small test-tube, upon which is a mark for 3 cubic centimetres, is then placed under *c*, the stopper at *a* is removed, and pure water is slowly dropped from a pipette upon the powdered glass. The blood solution is thus gradually displaced, and the washing is continued in this manner until the liquid in the test-tube amounts to 3 ccm. The tube is then taken away, several cubic centimetres of water are allowed to flow through the powdered glass, all the stoppers are inserted, *e* is connected with the aspirator, and when the excess of water has thus been removed the apparatus is ready for another experiment.

"The same powdered glass was used for from 50 to 60 determinations without it being necessary to renew it. The absorption apparatus contained originally 2 ccm. of dilute blood 1 : 40 ; hence the 3 ccm. now in the test-tube have a concentration of 1 : 60.

"Small rectangular bottles, with flat sides which are 0·5 cm. and 1 cm. wide, are very well suited to holding the blood solution for the observations with the spectroscope: these little bottles hold about 1·5 ccm. of solution, and are closed with carefully ground stoppers. One of these bottles is filled with the blood solution used in the experiment, and a second bottle is filled with the original blood solution, also diluted

to 1 : 60. One drop of ammonium sulphide is added to the contents of each bottle; the bottles are shaken, and after half an hour the spectra of the two solutions are examined, preferably by lamp-light, with a delicate pocket spectroscope.

"When the method is carried out as just described, it admits of a comparison of the two blood solutions under quite similar and at the same time the most favourable conditions as regards the concentration, the thickness of the observed column of liquid, the reducing agent, and the duration of the experiment. With respect to the lowest limit of the possible and certain detection of carbon monoxide in atmospheric air, I have, after many experiments, come to the same result as Hempel, viz., 0·03 per cent. At this concentration both bands are still distinctly recognisable. When the air contains less carbon monoxide, about 0·02 per cent, the presence of the gas is shown merely by a somewhat stronger absorption in the absorption spectrum, which now appears at *D* as a broad band, the maximum absorption of the reduced blood solution lying toward *E*. This observation is the last evidence, as Jäderholm has already stated in his admirable paper upon the lego-medical diagnosis of carbon monoxide poisoning, p. 22, which shows that some carbon monoxide is still present.

"It is very desirable to possess for these experiments a solution of blood which is clear, and which will keep for a long time, and the method proposed by Jäderholm (p. 30 of his article) answers the purpose excellently. He mixes together equal volumes of blood freed from fibrine, and of cold saturated borax solution. The addition of the borax prevents putre-

faction and does not change the spectroscopic properties of the blood, and reduction and combination with oxygen or carbon monoxide take place in the same manner as in fresh blood or hæmoglobin solution. The hæmoglobin gradually dissolves in the liquid, and, beginning at the bottom and proceeding upwards, the solution takes on a deep dark red colour. Such a solution of the colouring matter of blood in borax remains clear for months, and does not need to be filtered before being used for the spectroscopic examination. I have used this solution exclusively for my experiments, the desired concentration of 1 : 40 being obtained by mixing 1 ccm. of the solution with 19 ccm. of water. Even in this dilution, the solution will keep for several days.

"The permanence of the carbon monoxide reaction in this dilution, when the solution is kept in the small and tightly closed absorption bottles, is quite remarkable. I have kept solutions with 0·03 per cent and 0·05 per cent, together with the comparing solutions, for over three months without the reaction becoming less distinct.

"I will mention one other experiment which is of interest as serving to call attention to certain necessary precautions in the examination of the air of rooms filled with coal-gas.

"After the delicacy of the method had been proved by many experiments, it remained to test it also in a practical manner. For this purpose a small stove filled with burning charcoal was placed in a closed room in my laboratory, and the doors and openings into the chimney were closed. Into the room was passed a glass tube with a funnel-shaped mouth. This

tube was connected with a Mitscherlich bulb apparatus filled with water for washing the gas, and this was joined to a 10-litre bottle which aspirated the air. At the same time a 100 ccm. bottle, filled with water, was emptied in the same room, 3 ccm. of very dilute blood was put into it, and the walls of the bottle were rinsed for 3 to 4 minutes with this solution. Both experiments were begun after the charcoal had burned in the small room for about half an hour, at which time the air was stifling and of a peculiar acid odour, while what is commonly termed coal-gas was present in large amounts. Nevertheless the Vogel test showed no trace of carbon monoxide and, moreover, my method which had shown itself at other times to be so delicate, failed me completely, because all the colouring matter of the blood in the powdered glass was destroyed in a short time and the solution was consequently decoloured. It was evident, as was already shown by the slight bluish appearance in the bottle, that in spite of the interposed wash-bottle there had passed over those acid products of the decomposition and dry distillation of coal (perhaps phenol), which form when the coal is not completely burned, and which Hünefeld, in his work upon the legal tests for blood and carbon monoxide in blood,[1] has described in detail and has attempted to isolate.

"The bottle containing the remainder of the gas and some water was shaken several times and was allowed to stand until the next day; these substances were then absorbed, and 5 litres of the air still remaining in the bottle sufficed to give undoubted evidence of the presence of carbon monoxide. It would, however, be

[1] Leipsic, 1875, p. 40.

advisable to interpose a cylinder filled with coarse and moist powdered glass, and another filled with freshly slaked lime, as Wolffhügel has recommended."

Carbon monoxide may also be detected with sodium palladium chloride, metallic palladium being thrown down and the gas being changed to carbon dioxide. But palladium chloride is also decomposed by a large number of organic substances, and mistakes may arise from this cause.

Methane (CH_4).

Marsh-Gas—Fire-damp.

Specific gravity, 0·55297. Weight of 1 litre, 0·71549. According to Bunsen, 1 vol. of water absorbs at a temperature t,

$$0{\cdot}05449 - 0{\cdot}0011807t + 0{\cdot}0000102781t^2:$$

hence at

20°, 0·0349812 volume.

One vol. alcohol absorbs at temperature t,

$$0{\cdot}522586 - 0{\cdot}0028655t + 0{\cdot}0000142t^2:$$

hence at

20°, 0·47096 volume.

$$1 \text{ vol. } CH_4 = 2 \text{ vol. H} + \tfrac{1}{2} \text{ vol. C.}$$

Marsh-gas is always determined by combustion. One volume of methane unites with 2 volumes of oxygen, and 1 volume of carbon dioxide is formed.

To avoid the burning of nitrogen in the explosion, 100 volumes of incombustible gas are taken for from 25 to 37 volumes of the mixture of methane and oxygen (Bunsen).

No absorbent for marsh-gas is known.

Ethylene (C_2H_4).

Specific gravity, 0·96744. Weight of 1 litre, 1·25178.

$$2 \text{ vol. } C_2H_4 = 4 \text{ vol. H} + 2 \text{ vol. C.}$$

One volume of water absorbs at temperature t,

$$0{\cdot}25629 - 0{\cdot}00913631t + 0{\cdot}000188108t^2 :$$

hence at

20°, 0·1488 volume (Bunsen).

One volume of alcohol absorbs at $t°$,

$$3{\cdot}59498 - 0{\cdot}057716t + 0{\cdot}0006812t^2 :$$

hence at

20°, 2·7131 volumes (Carius).

Ether absorbs about twice its volume, turpentine oil and petroleum two and a half times their volumes, and olive oil its own volume of ethylene.

Either fuming sulphuric acid or bromine water is used for the absorption.

It is advisable to use sulphuric acid so concentrated that when the temperature is slightly lowered, crystals of pyrosulphuric acid will separate.

The analytical absorbing power is 8.

The acid is used in a simple pipette which has

three bulbs (Fig. 60). The small bulb is filled by the glass-blower with glass beads, which serve to give to the sulphuric acid the largest possible surface. With this arrangement the complete absorption of the heavy hydrocarbons, and of ethylene in particular, is effected by passing the gas into the pipette but once.

In this reaction some sulphur dioxide is usually formed, and, moreover, the vapour of fuming sulphuric acid has a very high tension, so that the gas residue, before being measured, must be freed from the acid vapours in the caustic potash pipette, a single passage of the gas into the pipette being also here sufficient.

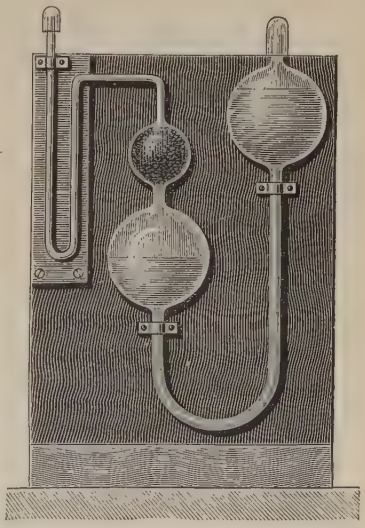

Fig. 60.

To avoid having the rubber connections between the pipette and burette attacked by the fuming sulphuric acid, the apparatus is so put together that the sulphuric acid does not quite fill the capillary of the pipette, and the connecting capillary is allowed to remain empty; the short rubber tube of the burette is also freed from liquid by means of a narrow tipped suction pipette, any reagent remaining in the rubber tube being first washed out by water with the same pipette. If care be taken that the sulphuric acid is stopped, after the

absorption, at the same point in the capillary at which it stood when the burette and pipette were first put together, then the small volume of air contained in the empty capillary tubes in the beginning causes, of course, no error in the determination of the heavy hydrocarbons or other gases, with the exception of nitrogen. In the nitrogen determination, allowance may be made for this air volume, but as each centimetre of the empty capillary corresponds to only 0·008 ccm., this value falls below the limit of the usual unavoidable experimental errors.

After the absorption, the rubber tube is taken off from the pipette, and the capillary and the larger tube are closed air-tight by little glass caps, which are pushed over narrow rubber rings placed upon the tubes.

Bromine is a good absorbent for ethylene. It is used in a pipette similar to the one just described. It is not necessary to fill the pipette completely with bromine, it being quite sufficient if a few cubic centimetres of bromine lie under water in the pipette. There is thus formed a saturated solution of bromine in water, which absorbs the ethylene. According to experiments of Cl. Winkler,[1] however, the absorption is not a complete one, and it is better to use fuming sulphuric acid for this purpose.

Acetylene (C_2H_2).

Specific gravity, 0·89820. Weight of 1 litre, 1·16219.

2 vol. C_2H_2 = 2 vol. H + 2 vol. C.

[1] *Zeitschrift für analyt. Chemie*, **28**, pp. 269-289.

Acetylene is somewhat soluble in water,[1] which dissolves its equal volume of the gas. Oil of turpentine and tetra-chlor-methane dissolve 2 volumes of the gas, amyl alcohol and styrol $3\frac{1}{2}$, chloroform and benzol 4, glacial acetic acid and alcohol 6. It is slowly absorbed by concentrated sulphuric acid, acetyl sulphonic acid being formed. An ammoniacal solution of cuprous chloride absorbs the gas rapidly, and there is formed a brown to violet-red precipitate of copper-acetylene, which explodes when heated or struck. Acetylene produces in an ammoniacal silver solution a white precipitate similar to the last, but even more explosive than the copper-acetylene. If the gas is led into ammoniacal solutions of aurous thiosulphate, or potassium mercuric iodide, exceptionally explosive compounds are formed.

All of the ammoniacal solutions of metals which have been mentioned may be used as absorbents for acetylene.

Although acetylene can be determined by combustion with oxygen, this method cannot usually be employed, because the gas occurs in mixtures with other combustible gases.

It is best determined by leading it through an ammoniacal cuprous chloride solution, a reddish-brown precipitate being thrown down. The precipitate is filtered off, and is washed with water containing ammonia until the wash-water passes through colourless.

Since copper-acetylene explodes at 95°, the acetylene is calculated from the copper oxide in the precipitate. The copper-acetylene has the composition

$$(C_2Cu_2H)_2O.$$

[1] The following details are taken from Winkler's *Anleitung zur chemischen Untersuchung der Industrie-Gase*, Part I. p. 109.

To determine the amount of copper present, hydrochloric acid is poured over the copper-acetylene, decomposing it with evolution of acetylene. As it is difficult to completely decompose the copper-acetylene, the end of the reaction is not waited for, but the rest of the precipitate, without being washed, is dried on the filter and ignited. The copper oxide is dissolved in a few drops of nitric acid, and this solution is added to the hydrochloric acid filtrate first obtained. The solution is then precipitated hot with sodium hydroxide, and the copper oxide is filtered off, ignited, and weighed.

Cyanogen (C_2N_2).

Specific gravity, 1·79907. Weight of 1 litre, 2·32784.

$$2 \text{ vol. } C_2N_2 = 2 \text{ vol. } C + 2 \text{ vol. } N.$$

One volume of water dissolves at 20°, 4·5 volumes of cyanogen; 1 volume of alcohol, 20 volumes of cyanogen.

Burned with twice its volume of oxygen it forms 2 volumes of carbon dioxide and 1 volume of nitrogen.

Caustic potash absorbs cyanogen, potassium cyanide and potassium cyanate being formed:

$$C_2N_2 + 2KOH = KCN + KCNO + H_2O.$$

Cyanogen is determined by absorbing it in a solution of potassium hydroxide, adding silver nitrate and then slightly acidifying with nitric acid. The precipitate is filtered off, converted into metallic silver by ignition in a porcelain crucible, and is then weighed.

Hydrocyanic Acid (HCN).

Specific gravity, 0·9359. Weight of 1 litre, 1·2096.

The gas is easily soluble in water and in alcohol. Potassium hydroxide absorbs it, potassium cyanide being formed.

Strong acids, especially hydrochloric acid and sulphuric acid, decompose hydrocyanic acid with formation of formic acid and ammonia.

To detect the acid,[1] add ferrous sulphate and one drop of ferric chloride to the solution of hydrocyanic acid or potassium cyanide, then add potassium hydroxide to alkaline reaction if the solution is not already alkaline, warm gently and acidify with hydrochloric acid. A dark-blue precipitate of Prussian blue results.

Another test for hydrocyanic acid is to add ammonium sulphide until the solution takes on a yellow colour, then ammonia,—or, better, a drop of sodium hydroxide,—and to heat the solution until the excess of ammonium sulphide has been driven off and the solution is again colourless. In this way there is formed either ammonium or sodium sulphocyanate, which, after acidifying, gives the characteristic blood-red colour with ferric chloride.

Hydrocyanic acid is determined by absorbing it with a solution of potassium hydroxide and precipitating it with silver nitrate, exactly as given for cyanogen.

The reactions are as follows:—

$$HCN + KOH = KCN + H_2O,$$
$$KCN + AgNO_3 = AgCN + KNO_3,$$
$$CN = Ag.$$

[1] Cl. Winkler, *Anleitung zur chemischen Untersuchung der Industrie-Gase*, Part I. p. 60.

Hydrogen Sulphide (H_2S).

Specific gravity, 1·17697. Weight of 1 litre, 1·52290.

$$2 \text{ vol. } H_2S = 2 \text{ vol. } H + 1 \text{ vol. } S.$$

According to Bunsen's experiments, water absorbs—

At	2°	C.,	4·2373 vol. H_2S
„	9·8°	„	3·5446 „ „
„	14·6°	„	3·2651 „ „
„	19°	„	2·9050 „ „

Between 2° and 43·3° the absorption by 1 vol. water at $t°$

$= 4{\cdot}3706 - 0{\cdot}083687t + 0{\cdot}0005213t^2$ volumes of H_2S.

According to the same authority alcohol takes up, between 1° and 22°, at temperature t,

$$17{\cdot}891 - 0{\cdot}65598t + 0{\cdot}00661t^2 \text{ volumes.}$$

$1\frac{1}{2}$ volumes of oxygen are necessary for the combustion of 1 volume of hydrogen sulphide, and 1 volume of sulphur dioxide is formed.

When sulphur trioxide is brought into contact with hydrogen sulphide, sulphuric acid, sulphur dioxide, and sulphur result—

$$2SO_3 + H_2S = H_2SO_4 + SO_2 + S.$$

Potassium hydroxide and solutions of many of the heavier metals absorb hydrogen sulphide, and give the corresponding compound.[1]

If hydrogen sulphide is present in any considerable amount, its presence is shown by its odour. A surer

[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part I. p. 60.

test is to introduce into the gas a strip of so-called lead-paper. The paper becomes covered with a glistening brownish-black layer of lead sulphide, even when only traces of hydrogen sulphide are present.

Concentrated nitric acid and solutions of chromic acid, permanganic acid, ferric oxide, chlorine, bromine, iodine, and of the oxygen acids of the last three, decompose hydrogen sulphide immediately, with the separation of free sulphur; in the presence of an excess of the halogens, the sulphur is finally attacked and wholly or partly converted into sulphuric acid.

Hydrogen sulphide may be quantitatively determined by Dupasquier's method, a measured quantity of gas (see Fig. 43) being drawn through a solution of iodine in potassium iodide, to which some starch paste has been added. The operation is stopped as soon as the solution becomes colourless. The reaction is—

$$H_2S + I_2 = 2HI + S,$$

but the reaction follows this equation precisely only when the solutions are very dilute and protected from direct sunlight.

R. Fresenius[1] determines hydrogen sulphide gravimetrically by first drying the gases with calcium chloride and then absorbing the hydrogen sulphide in U-tubes which are filled $\frac{5}{6}$ with pumice-stone impregnated with copper sulphate, and $\frac{1}{6}$, at the exit end, with calcium chloride. The pumice-stone is prepared as follows:—Place 60 grams of pumice-stone, in pieces the size of a pea, in a small porcelain dish,

[1] R. Fresenius, *Anleitung zur quant. Analyse*, 6th ed., Part I. p. 505. Also *Zeitschr. f. analyt. Chemie*, **10**, 75.

and pour a hot concentrated solution of from 30 to 35 grams of copper sulphate over it. Evaporate the solution to dryness with constant stirring, place the dish in an air- or oil-bath, whose temperature is kept between 150° and 160° C., and let it remain there four hours.

A tube containing 14 grams of this copper sulphate pumice-stone takes up about 2 grams of hydrogen sulphide. To make sure of complete absorption two such tubes should always be used. When the pumice-stone is less thoroughly dried, it takes up a much smaller amount of hydrogen sulphide, and when it has been dried at a higher heat—until it has lost its water of crystallisation—it causes a decomposition of the hydrogen sulphide and the evolution of sulphur dioxide.

Hydrogen sulphide can also be determined by passing the gas through a solution of bromine in water, precipitating the sulphuric acid thus formed with barium chloride, and weighing as barium sulphate.

According to Bunsen[1] it is possible to determine the hydrogen sulphide of a gas mixture containing hydrogen, nitrogen, carbon dioxide, hydrocarbons, etc., by means of balls of manganese dioxide. The purest pyrolusite is ground to a very fine powder, and is then stirred with sufficient distilled water to make a thin paste. The balls are made from this paste by pressing it in a bullet-mould which has been rubbed with oil. The balls are dried in an air-bath, and are then covered with a concentrated sirupy solution of phosphoric acid.

[1] Bunsen, *Gasometrische Methoden*, 2d ed., p. 111.

Sulphur Dioxide (SO_2).

Specific gravity, 2·21295. Weight of 1 litre, 2·86336.

$$2 \text{ vol. } SO_2 = 1 \text{ vol. } S + 2 \text{ vol. } O.$$

Sulphur dioxide is easily soluble in water. According to Sims, 1 volume of water dissolves at 760 mm. pressure—

At 7°,	61·65	vol. SO_2
„ 20°,	36·43	„ „
„ 39·8°,	20·5	„ „
„ 50·°,	15·62	„ „

One volume of water absorbs at 76 cm. pressure, and at temperatures between 0° and 20°, at $t°$,

$$79·789 - 2·6077t + 0·029349t^2$$

volumes of sulphur dioxide; hence 1 volume of the saturated aqueous solution contains, at $t°$,

$$68·861 - 1·87025t + 0·01225t^2$$

volumes of the gaseous acid.

For temperatures between 21° and 40°, the coefficient of absorption is—

$$75·182 - 2·1716t + 0·01903t^2,$$

and the amount of gas contained by the saturated aqueous solution is—

$$60·952 - 1·38898t + 0·00726t^2 \text{ volumes.}$$

In the solution which has been saturated at 0°, a

hydrate separates out in crystals. These crystals melt between 1° and 2° with evolution of gas, and probably have the formula

$$H_2SO_3 + 14H_2O.$$

The solution of the gas has a strong acid reaction and reddens blue litmus paper. This the completely dry gas does not do, because sulphurous acid, H_2SO_3, is formed only when the gas unites with water.

The gas is condensed by pressure or cold to a colourless mobile liquid which boils at $-8°$.

One vol. of alcohol absorbs at 760 mm. pressure and $t°$, $328{\cdot}62 - 16{\cdot}95t + 0{\cdot}3119t^2$ volumes of sulphur dioxide. The specific gravity of the solution is then—

$$1{\cdot}11937 - 0{\cdot}014091t + 0{\cdot}000257t^2 \text{ (Carius).}$$

The alcoholic solution of sulphur dioxide, saturated at 0°, contains 216·4 volumes of the gas.

Alkalies absorbed the gas very actively, with evolution of heat.

Sulphur dioxide is determined either by leading a measured volume of the gas through a solution of bromine in water, and precipitating the sulphuric acid thus formed by barium chloride, or by measuring the amount of gas required to decolorise an iodine solution of known strength.

In the latter method the reaction, when it takes place in aqueous solutions, follows this equation—

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI,$$

so long as the liquid does not contain more than 0·04 per cent of sulphur dioxide (Bunsen).

Reich has applied this method to the determining of sulphur dioxide in the gases from roasting furnaces (see p. 249).

1 ccm. $\frac{N}{10}$ iodine solution = 0·0032 grams = 0·11 ccm. SO_2.

Carbon Oxysulphide (COS).

Specific gravity, 2·07483. Weight of 1 litre, 2·68464.

2 vol. COS = 1 vol. C + 1 vol. O + 1 vol. S.

Water absorbs about its own volume of the gas, and takes on its odour and sweet, sharp taste. The gas is probably present in many sulphur springs.

One volume of carbon oxysulphide needs $1\frac{1}{2}$ volume of oxygen for its combustion, and yields 1 volume of CO_2 and 1 volume of SO_2. The mixture explodes with a loud sound and a brilliant white flame. With $7\frac{1}{2}$ volumes of air it burns quietly.[1]

If carbon oxysulphide is led through heated alkaline earths, alkalies, or a layer of red-hot soda lime, it is wholly absorbed—

$$COS + 2CaO = CaS + CaCO_3.$$

A platinum wire heated to redness by an electric current converts the gas, without change of volume, into sulphur and carbon monoxide.

Potassium hydroxide in aqueous or alcoholic solution absorbs the gas only very incompletely (Winkler).

Alkaline lead solutions and ammoniacal silver solutions act similarly.

[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part I. p. 111.

The gas is rapidly and completely absorbed by a solution of one part of potassium hydroxide in two parts of water, mixed with an equal volume of alcohol.[1]

Chlorine (Cl).

Specific gravity, 2·44921. Weight of 1 litre, 3·16906.

Chlorine is quite soluble in water. One part of cold water dissolves approximately two volumes of chlorine; hot water dissolves less. Experiments by Roscoe have shown that the absorptions do not follow the usual laws of absorption. According to Schönfeld, one volume of water absorbs the following volumes of chlorine—

10°,	2·5852
15°,	2·3681
20°,	2·1565
25°,	1·9504
30°,	1·7499
35°,	1·5550
40°,	1·3656

Chlorine is best determined by the Bunsen procedure, in which the gas is led through a solution of potassium iodide, and the iodine set free is titrated with sodium thiosulphate—

$$Cl_2 + 2KI = 2KCl + I_2,$$
$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

Chlorine can also be absorbed with potassium hydroxide or caustic soda. In cold dilute solutions potassium hypochlorite is formed—

[1] Klason, *Jour. f. prakt. chemie*, N. F. **36**, pp. 64 to 74.

$$2KOH + Cl_2 = KClO + KCl + H_2O.$$

In hot concentrated solutions, the reaction is—

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

According to R. v. Wagner, the hypochlorite formed may, after addition of potassium iodide and hydrochloric acid, be titrated with sodium thiosulphate.

If a solution contains free chlorine together with hydrochloric acid, they may both be determined in the following manner (Fresenius) :—

To a weighed portion of the liquid add an aqueous solution of sulphurous acid until the latter is in excess; after some time add nitric acid and then some potassium chromate to destroy the excess of sulphur dioxide, and precipitate the total chlorine as silver chloride.

If now the amount of free chlorine is determined in a second portion by potassium iodide, the difference gives the quantity of chlorine present in the form of chloride.

The total chlorine may also be volumetrically determined by absorbing the gases with a solution of sodium hydroxide, adding sulphur dioxide, then, after a while, nitric acid and some potassium chromate, and finally neutralising the solution by adding calcium carbonate. All chlorine is now present as chloride, and the solution is neutral, so that the chlorine may be titrated with a neutral silver solution, potassium chromate being used as indicator.

Hydrochloric Acid (HCl).

Specific gravity, 1·25922. Weight of 1 litre, 1·62932.

2 vol. HCl = 1 vol. Cl + 1 vol. H.

Hydrochloric acid dissolves very easily in water, in ice, and in salts containing water of crystallisation, as Glauber's salt, copper sulphate, magnesium sulphate, borax, etc.

According to Roscoe and Dittmar, 1 volume of water dissolves at 0°, 503 volumes of the gas. The parts by weight of the gas which dissolve in one gram of water at a pressure of 760 mm. and at different temperatures, are given in the following table :—

Temperature.	HCl.	Temperature.	HCl.
0	0·825	32	0·665
4	0·804	36	0·649
8	0·783	40	0·633
12	0·762	44	0·618
16	0·742	48	0·603
20	0·721	52	0·589
24	0·700	56	0·575
28	0·682	60	0·561

At ordinary temperatures, 1 volume of alcohol dissolves 327 volumes of hydrochloric acid.

At a pressure of from 30 to 40 atmospheres, the gas condenses to a colourless liquid of strong refractive power.

If no other acid gas is present with the hydrochloric acid, it can be determined by drawing a measured quantity of the gas through a standardised solution of an alkali and titrating back with an acid.

Hydrochloric acid may be accurately determined by absorbing it with an alkaline solution free from chlorine, and, after acidifying, precipitating it with silver nitrate, and weighing as silver chloride.

A method proposed by Cl. Winkler,[1] and based upon J. Volhard's volumetric method for the determination of silver,[2] consists in placing in a suitable absorption apparatus a few drops of ammonium sulphocyanate or potassium sulphocyanate, some iron alum solution, and a measured amount of $\frac{N}{10}$ silver nitrate solution. Upon leading the gas through this solution the hydrochloric acid unites with the silver, forming silver chloride. The end of the reaction is shown by the blood-red colour. The cause of this colour is, that after all of the silver nitrate has been changed to silver chloride, the silver sulphocyanate present is also decomposed and ferric sulphocyanate is formed. The volume of the gas is measured and the amount of hydrochloric acid it contains is calculated.

Silicon Tetrafluoride (SiF_4).

Specific gravity, 3·60469. Weight of 1 litre, 4·66414.

2 vol. SiF_4 = 1 vol. Si + 4 vol. F.

The gas is completely taken up by water, being at the same time decomposed—

$$3SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6.$$

[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II. p. 322.

[2] J. Volhard, *Zeitschrift für analyt. Chemie*, **13**, 171, and **17**, 482.

This reaction, which has been employed by R. Fresenius[1] for the quantitative determination of fluorine, might possibly be made use of for the determination of silicon tetrafluoride in gases: up to the present time, however, no satisfactory method has been devised. The silicon tetrafluoride probably formed in fusion processes is always mixed with large amounts of steam, dust, and sulphur dioxide, and for these reasons its determination is exceptionally difficult.

Phosphine (PH_3).

Specific gravity, 1·17552. Weight of 1 litre, 1·52102.

$$2 \text{ vol. } PH_3 = \tfrac{1}{2} \text{ vol. } P + 3 \text{ vol. } H.$$

Phosphine is a colourless gas with a very unpleasant odour, resembling that of decayed fish. It is very poisonous. The pure gas takes fire only at a temperature above 100°, but the friction of the stopper of the bottle containing the gas is often sufficient to ignite it.

It can be mixed with pure oxygen without change, but if the mixture be suddenly brought under diminished pressure it explodes. Phosphine takes fire when brought in contact with a drop of fuming nitric acid, or with the vapour of chlorine or bromine.

Phosphine is somewhat soluble in water. One volume of water absorbs about 0·02 volume of the gas, and takes on its odour and disgusting taste. Exposed to the light, the solution decomposes with evolution of hydrogen and separation of amorphous

[1] Fresenius, *Quant. chemische Analyse*, 6th ed., Part I. p. 431.

phosphorus. The gas is decomposed by electric sparks into phosphorus and hydrogen, the resulting volume being exactly $1\frac{1}{2}$ times that at the beginning.

Phosphine combines, as does ammonia, with metallic chlorides, aluminium chloride, tin chloride, and antimony chloride.

The gas cannot be detected by means of lead-paper, but strips of paper impregnated with silver nitrate are turned black at once, metallic silver separating out and phosphoric acid being formed.

Phosphine can be determined by drawing the gas in question through bromine water and then precipitating the resulting phosphoric acid by magnesia mixture. If a silver solution has been used for the absorption, the excess of silver must first be removed by hydrochloric acid.

The phosphoric acid thus formed may also be detected with ammonium molybdate.

According to J. Riban[1] a hydrochloric acid solution of cuprous chloride absorbs phosphine.

Arsine (AsH_3).

Specific gravity, 2·69728. Weight of 1 litre, 3·49003.

2 vol. $AsH_3 = \frac{1}{2}$ vol. As + 3 vol. H.

Arsine is a colourless gas of very unpleasant odour. It burns with a blue flame, with formation of white clouds of arsenic trioxide. When passed through a highly heated tube, the gas is decomposed and a glistening mirror of metallic arsenic is deposited.

[1] *Compt. rend.* **88**, 581.

When arsine is led over red-hot copper oxide, water and copper arsenide are formed. Arsine may be easily detected in this manner. If arsine is passed over heated metals, such as tin, potassium, or sodium, arsenides are formed and hydrogen is set free.

Arsine precipitates the metal from solutions of gold and silver salts—

$$AsH_3 + 6AgNO_3 + 3H_2O = As(OH)_3 + 6HNO_3 + 6Ag,$$

and if an aqueous solution of ammonia be carefully added to the filtrate, a yellow ring of silver arsenite is formed. Minute quantities of arsenic may be detected in this manner.

Water absorbs five times its volume of arsine.

Bromine, chlorine, and iodine decompose the gas.

A very suitable method for the determination of arsine consists in leading it into a silver solution, precipitating the excess of silver by hydrochloric acid, filtering, and, after warming, precipitating the arsenic with magnesia mixture. The precipitate is ignited and weighed as $Mg_2As_2O_7$.

Arsine can be completely removed from hydrogen sulphide by leading the mixture of the two gases through a tube which contains pieces of iodine.

Stibine (SbH_3).

Specific gravity, 4·3287. Weight of 1 litre, 5·6.

$$2 \text{ vol. } SbH_3 = \tfrac{1}{2} \text{ vol. Sb} + 3 \text{ vol. H.}$$

Water absorbs from 4 to 5 volumes of the gas at

10°. Stibine burns with a greenish flame, and gives off white fumes of antimony trioxide.

If the gas be led through glass tubes heated to redness, metallic antimony is deposited in the form of a mirror a short distance beyond the heated point.

If stibine be passed into a solution of silver nitrate, black silver antimonide, $SbAg_3$, mixed with metallic silver, is precipitated.

Sulphur, when exposed to the light, or when heated to above 100°, decomposes the gas and becomes coated with orange-red antimony sulphide—

$$2SbH_3 + 6S = Sb_2S_3 + 3H_2S.$$

Hydrogen sulphide acts similarly in the light—

$$2SbH_3 + 3H_2S = Sb_2S_3 + 6H_2.$$

Concentrated nitric acid and potassium permanganate oxidise the gas. Stibine does not blacken lead-paper.

Stibine may be determined by leading the gas under examination into a silver solution, filtering off the silver antimonide formed, and digesting it with ammonium sulphide. The antimony goes into solution as ammonium sulphantimonite, and after being thrown down again, it can be weighed as antimony sulphide, or it may be converted into antimony tetroxide and weighed as such.

PART III

PRACTICAL APPLICATIONS OF GAS ANALYSIS

CHAPTER I

COMBUSTION GASES—FURNACE GASES

In many industries the profits are largely dependent upon the amounts paid out for fuel, so that in all factories having large furnaces a systematic examination of the working of the furnace is of considerable importance. The driving of a fire is the more favourable the less the excess of air beyond the amount necessary for producing complete combustion. In many boiler plants which seem to be otherwise well constructed, the examination shows that an enormous excess of air is being used, and that a correspondingly large amount of heat is being allowed to pass unused into the chimney. It is impracticable to wholly abstract the heat from the gases from the fire; a certain amount of heat must be left in them, so that they will move rapidly enough in the chimney. It follows that a disproportionately large amount of heat will be lost when the draught in the furnace is too strong. Even the most skilful stoker will not be able to tell merely from the appearance of the fire, exactly how the combustion is proceeding. For these reasons it is advis-

able to adopt some arrangement which will continually draw off a small current of gas from the fire, and to give the stoker a bonus which is

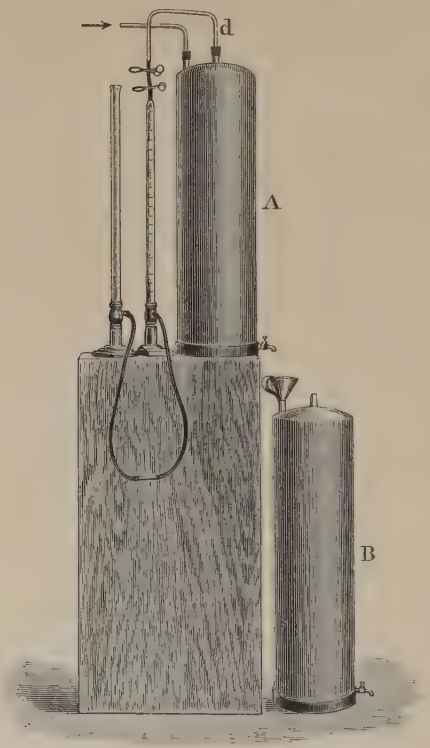

Fig. 61.

higher the less oxygen there is in the departing gases.

To judge of the combustion, it is quite sufficient to make merely a determination of the oxygen, for the amounts of all other products of combustion

are of course dependent upon the oxygen, provided that the furnace is not giving off thick clouds of smoke, *i.e.* that, instead of burning, the fire merely smoulders.

The tube for taking off the gases is introduced into the flue at a place which is selected with reference to the points mentioned on p. 3. It is convenient to connect the tube with a bottle aspirator made of ordinary sheet-zinc (see Fig. 61). The water is allowed to drop from *A* into *B*, and its flow can easily be so regulated that the water will flow out of *A* once in 6, 12, or 24 hours. The analysis of this gas sample gives the average composition of the furnace gases. The tube *d*, which reaches to about the middle of *A*, serves for taking off samples with the gas burette.

Well-managed furnaces should give not more than about 8 per cent of free oxygen. The furnaces of the present day may be said to be exceptionally good when the gases from the fire contain only from 3 to 4 per cent of oxygen.

If a more complete analysis of the furnace gases is desired, the procedure is exactly the same as that given for the analysis of generator gases.

Furnace gases usually contain only carbon dioxide, oxygen, and nitrogen. All other gases are present in but very small amounts. In oft-repeated analyses the author has always found only traces of carbon monoxide, methane, and the heavy hydrocarbons.

The apparatus necessary for thus controlling the working of a furnace is—

1. A bottle aspirator, with the necessary tubes, for collecting the gas.

2. A simple gas burette.

3. A pipette for solid absorbents, which is filled with phosphorus and kept in a light-tight box.

CHAPTER II

ILLUMINATING GAS

Water Gas—Generator Gas—Blast-furnace Gases—Coke-furnace Gases.

The gases formed in dry distillation of coal are quantitatively of very different composition. All of them contain hydrocarbon vapours, carbon dioxide, carbon monoxide, heavy hydrocarbons, marsh-gas, hydrogen, water, and nitrogen, and most of them contain also some oxygen which has entered through leakages in the apparatus.

The unpurified gas contains hydrogen sulphide, ammonia, uncondensed tar, as well as carbon disulphide and organic sulphur compounds.

In the examination of illuminating gas there must be made—

1. A photometric measurement of the illuminating power of the gas.

2. The determination of the specific gravity of the gas.

3. The determination of tar and the constituents separable by cooling.

4. The volumetric analysis of the gaseous constituents.
5. The determination of sulphur.
6. The determination of ammonia.
7. The determination of carbon dioxide.

1. *The Measurement of the Illuminating Power.*

The amount of light generated by an illuminating gas in burning is dependent upon the construction of the burner, so that this determination is accompanied by large errors.

Up to the present time there exists no perfectly accurate and simple method for determining the illuminating power of a flame. When we remember that the light given out by ordinary lamps is composed of a great number of rays of different colours which result from their different wave-lengths, and which cannot be directly compared with one another, it is easy to understand that the results of the determinations are, under certain conditions, quite variable.

If candle flames and gas flames are compared, the photometric measurements agree quite satisfactorily. If, however, the yellow light of a candle be compared with the white light of a Siemens regenerative burner, an electric lamp, or an Auer von Welsbach incandescent light, one will find it quite impossible to make even approximately accurate measurements, and the uncertainty in the determination will amount to more than a whole candle power. The explanation of this is, that while similarly coloured sources of light may be directly measured in the photometer, lights of

different colours cannot be compared with one another. The electric light, which is rich in blue rays, cannot be compared with a candle flame, which possesses but few of these rays. The coloured rays are not of equal value for purposes of illumination, and a correct idea of the lighting power of any appliance can be obtained only by breaking up the light by means of a spectro-photometer, and then ascertaining how much of each sort of light is present. Several spectro-photometers for purely scientific researches have been devised.

For controlling the working of gasworks, the measurement of illuminating power is nevertheless of great value, because it can be quickly made. But it should not be forgotten that only gases of similar composition can be compared with one another. If one wished to compare oil-gas with ordinary illuminating gas, he would immediately be confronted by the difficulty that there is no burner in which both gases can be burned with equal advantage. For this reason the kind of burner in which the gas was burned should be exactly stated in all photometric measurements.

For ordinary illuminating gas the so-called normal burner of Elsler has been adopted in Germany. This is an Argand burner consuming 150 litres per hour, and which must show, when burning, a pressure of 2·5 mm. in the burner.

The unit of light in use in Germany is a candle of paraffin with melting point 55° C. The candle has a diameter of 20 mm., and six of them weigh 500 grams. The wick, which weighs 0·668 grams per metre, consists of twenty-four cotton threads, one of which is red so that the candles may be easily

distinguished. The height of the flame is 50 mm.

Instead of this candle an amyl acetate lamp of the Hafner-Alteneck construction is sometimes used. An advantage possessed by the amyl acetate lamp is, that when once it has been regulated it burns without change for a long time, while, with a candle, the

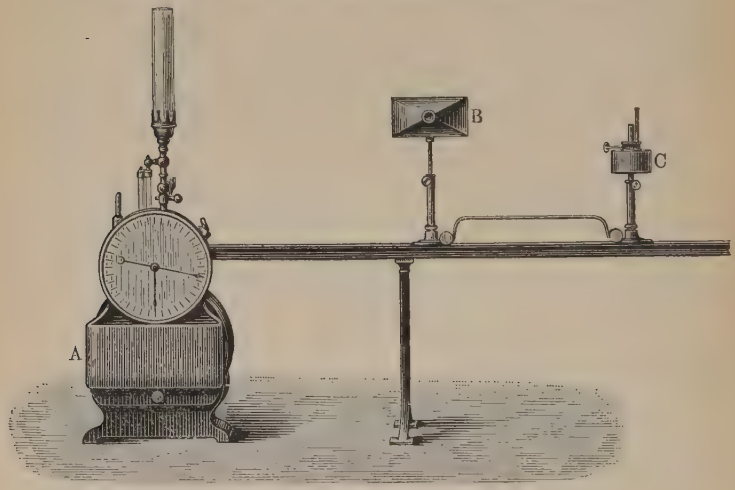

Fig. 62.

height of the flame must be constantly regulated by cutting off the wick. 1000 of the above candles are equal to 977 of the English spermaceti candles, and to 102 Paris Carcel-lamps.

The measurement of the illuminating power is made with a Bunsen photometer (Fig. 62). This consists of a partly translucent screen of paper, which can be moved back and forth between the normal light and the flame under examination. In measuring,

the screen is brought into such a position that the translucent spot appears equally dark on both sides, the observation being easily made by means of two mirrors in *B*, placed at the proper angles.

In this position the screen is illuminated with equal intensity by the two sources of light. The ratio between the illuminating power of the flame that is being tested and that of the normal flame, is as the squares of the distances of the flames from the screen.

The photometer is usually so arranged that the normal flame is fastened, at a definite distance from the screen, to a slide which moves along a track. On this track is a scale, from which the illuminating power may be directly read off.

The paper screen is best made from fine white drawing-paper that does not glisten, and that is about as thick as ordinary writing-paper. A cork is dipped into molten paraffin, stearin, or spermaceti, and is then pressed upon the middle of the paper. When the fat has cooled it is scraped off with a knife, and the paper is warmed until the spot appears uniformly translucent. If it is too nearly transparent, the paper is laid between two sheets of clean blotting-paper, and pressed with a warm flat-iron.

The photometer has lately been improved,[1] the fat spot being replaced by an optical arrangement consisting essentially of two prisms, by means of which the light from one source appears as a spot surrounded by the light from the other source. In this way a very

[1] O. Lummer and E. Brodhun, "Ersatz des Photometerfettflecks durch eine rein optische Vorrichtung." *Zeitschrift für Instrumentenkunde*, 1889, pp. 23 and 41.

sharp comparison of the illuminating powers of the two flames is made possible.

To determine the candle power of an illuminating gas, the consumption of the flame is first brought to 150 litres per hour by means of an experimental gas-meter. The flame of the normal candle or amyl acetate lamp having been brought to the proper height, the photometric measurement is made.

The measurement should be made in a room with blackened walls, and with windows which can be covered light-tight by black curtains. The room itself should be dry and well ventilated, since the accumulation of carbon dioxide changes considerably the illuminating power of a flame. The gas passing to the normal burner must never be led through long pieces of rubber tubing, because they would change its illuminating power.

Unless the gas-meter is in constant use, the gas must burn in the normal burner for at least two hours before the measurement is made.[1]

2. *The Determination of the Specific Gravity.*

The determination of the specific gravity is most conveniently made by Bunsen's method[2] of measuring the speed of escape of the gas.

This method is based upon the fact that the specific gravities of two gases escaping through narrow openings in thin plates bear nearly the same ratio to each other as the squares of their speeds of escape. If a gas

[1] Given in detail in N. H. Schilling's *Handbuch für Steinkohlengas-Beleuchtung.*

[2] Bunsen, *Gasometrische Methoden*, 2d ed., p. 184.

of the specific gravity s has a speed of flow t, and another gas of a specific gravity s_1 has a speed of flow t_1, the relation between the speed of escape and the specific gravity is given by the equation—

$$\frac{s_1}{s} = \frac{t_1^2}{t^2}.$$

If s or the specific gravity of one of the gases be regarded as 1, the specific gravity of the other gas is found by the formula—

$$s_1 = \frac{t_1^2}{t^2}.$$

Fig. 63 shows the apparatus used for this determination. A glass tube of about 70 ccm. capacity is luted into the iron cap A. This cap is fitted with a three-way stopcock by means of which the inside of the glass tube can be brought into communication with either the tube B, through which the gases are introduced, or the small opening in C. This opening is made in a platinum plate, which is about as thick as tin foil, and is luted in position. To obtain a platinum plate as thin and an opening as small as possible, the platinum foil is pierced with a fine sewing needle, and is hammered with a polished hammer upon a polished anvil until the opening can no longer be seen with the naked eye, and is only visible when the plate is held between the eye and a bright flame. The plate thus perforated is cut out in the form of a small circular disc, the opening being at the centre.

In order that the gases to be examined may always escape through the opening C under the same conditions

as regards pressure, there is placed in A a float bb. This float should be as light as possible, and for this reason it is best made from a very thin-walled glass tube. The float has at β a little button of black glass from which projects a small, white glass point.

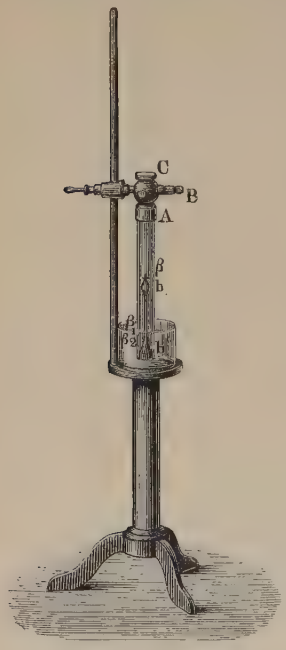

Fig. 63.

Two fine threads of black glass, β_1 and β_2, are fused around the lower part of the stem of the float. These two threads, together with the black glass button at the top, serve as marks.

If the tube containing the gas be pushed down so far into the mercury that a mark on the glass is tangent to the outer mercury surface, then the float which is inside the tube is no longer visible through the telescope.

If now the stopcock be opened and the gas allowed to escape through the opening in the platinum plate, the float rises, being carried up upon the surface of the mercury in the tube. If the level of the external mercury be observed through the telescope, the white glass tip of the float soon comes into the field, and informs the observer that the black button β will shortly appear. When this comes in sight the time is taken, the end of the timing being at that moment at which the mark β_2 comes into the field of

the telescope; the near approach of β_2 is here shown by the appearance of β_1.

From these observations is obtained the rapidity of escape of a column of gas which, measured from β, has the length shown by the marks $\beta\beta_2$ on the float: moreover, the gases escape under the same differences of pressure in all of the experiments. The times taken by the different gases to escape through the fine opening in C give, when squared, the ratios of the specific gravities of the gases.

The gases must be dried, and the mercury must be pure and dry. An advantage of the Bunsen apparatus is that a determination can be made with a very small quantity of the gas.

N. H. Schilling has given the apparatus a very practical form for the examination of illuminating gas, where large amounts of the gas are usually available.

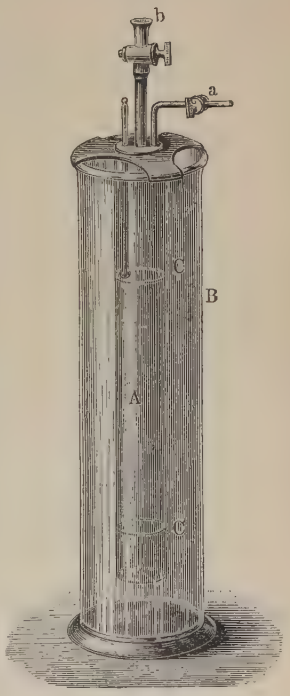

Fig. 64.

A (Fig. 64) is a glass tube of 40 mm. internal diameter and about 450 mm. long. The upper end is luted into a brass cover into which is inserted the tube a through which the gas is led in. In the middle of the plate is the escape tube b, and through another

opening passes a thermometer. On the end of *b* is the perforated platinum plate. The inner cylinder has two marks, *CC*. The apparatus is filled with water.

To determine the specific gravity of an illuminating gas with this apparatus, the tube is first filled with air, and the time of escape of the air, under the prevailing temperature and pressure, is noted. The last trace of

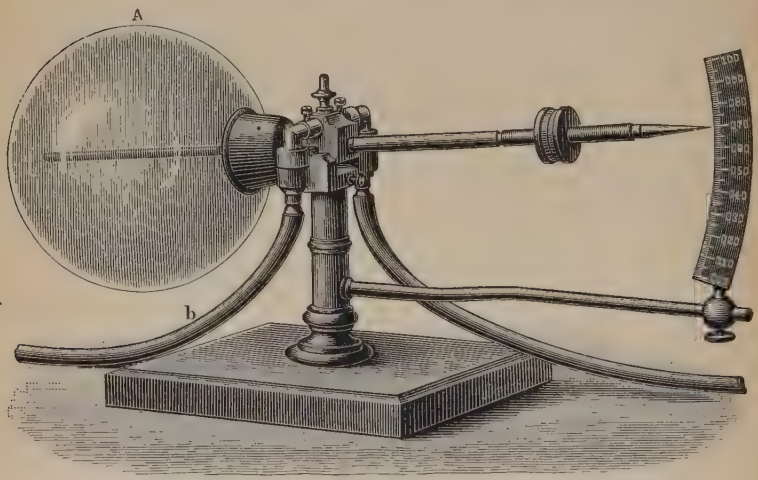

Fig. 65

air is then removed by repeatedly drawing in and driving out the gas to be examined, and the time of escape of the illuminating gas is then observed. The squares of the values are directly proportional to the specific gravities of the gases. Since the specific gravity of air is usually taken as 1, the calculation is very simple.

A very convenient arrangement for the continuous

and direct determination of the specific gravity is the gas-balance of Friedrich Lux.[1]

The instrument (Fig. 65) consists of a large bulb *A*, which is attached to one end of a lever; the other end gives directly on a scale the specific gravity of the gas. The lever is so made that the gas to be examined can be led through the tube *b* and through the hollow support into the bulb. The gas passes off through a second tube which is also connected with the fulcrum of the lever. If a number of such balances are joined together, and if, between the balances, absorption apparatus for the various constituents is introduced, the composition of the gas can be read off directly from the positions of the different pointers. For use of this sort, Lux has devised a balance with two bulbs, by means of which the amount of one constituent in the gas can be directly read off.

The results obtained by this instrument are of course influenced by the temperature and the variations of pressure, but nevertheless the apparatus is very well adapted for controlling the working of a gas plant.

3. *The Determination of Tar, etc.*

For the determination of tar in unwashed gases, F. Tieftrunk uses the apparatus shown in Fig. 66. Winkler[2] describes this as follows:—

"The glass cylinder *A* has a brass rim, and it can be tightly closed by means of a plate which is fastened with screws. To the tube *c* is attached a bell-shaped

[1] To be obtained from Friedrich Lux, Ludwigshafen, Germany.

[2] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II. p. 52.

device *h*, which consists of perforated sheets of brass slipped over the tube. The distance between the rows of holes and also between the holes themselves is about 5 mm. The glass cylinder *A* is filled somewhat more than half full of alcohol of from 25 to 29 per cent by weight, the bell being entirely covered by the liquid. The alcohol takes up the tar which enters, but is said

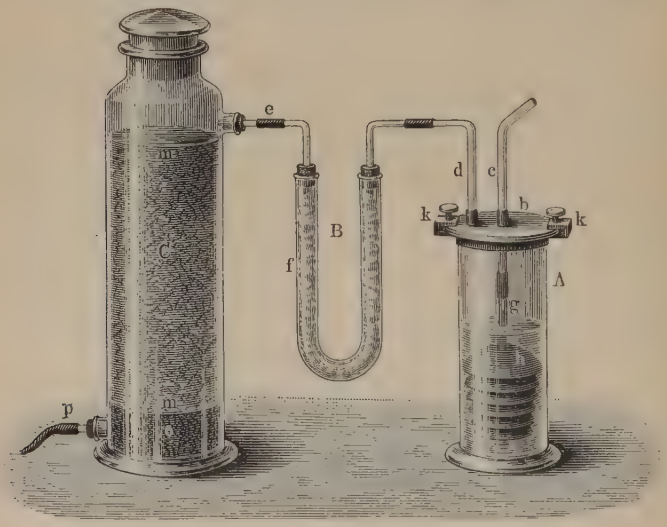

Fig. 66.

to hold back only traces of other constituents, such as benzene and naphthalene.

"The U-tube *B* is 12 mm. in diameter and 10 cm. long, and is filled with cotton. *C* is a glass-stoppered cylinder with two side openings. The lower part *o* of the cylinder is filled with cellulose; upon this lies a sheet of coarse filter paper, and above that is a layer of bog-iron ore, *mm*.

"The gas enters at *c* and passes out through *p* into an experimental gas-meter, and then into the aspirator. Before beginning the experiment, purified illuminating gas is allowed to pass through the washing apparatus for ten minutes to destroy the surface adhesion.

"The cotton in *B* should not be at all brown at the end of the experiment; if it is, it must be extracted with carbon disulphide.

"The solution thus obtained is placed in a weighed dish, and is allowed to evaporate. According to Tieftrunk's experience, one third of the total oil passes off at the same time, and a correction is made for this after the residue has been weighed.

"When the experiment is ended, the apparatus is taken apart, the lid of the vessel *A* is raised, the tar adhering to the bell *h* is washed down with the aid of a wash-bottle filled with alcohol of 35° Tr., and the whole is allowed to stand for twelve hours. The solution is then filtered through a dried and weighed filter; the aspirator is used in this operation, but care is taken to turn it off when, toward the last, the liquid tar is brought upon the filter. After washing, the filter and its contents are placed in a desiccator, and after drying for twelve hours both are weighed. The weighing of the filter with and without the tar may conveniently be performed in a glass dish with steep sides. Some particles of tar remain clinging to the bell and the walls of the glass cylinder, in spite of the washing. As this cannot be avoided, the amount of tar adhering to the glass is determined by putting the apparatus—whose original weight must be known—together again, and drawing 100 litres of dry air through it. By this current of air, which lasts for

about forty minutes, all water adhering to the walls is surely driven out, and the increase of weight of the apparatus gives the amount of the adhering tar. The weighings are made on a balance which, with a load of 1 kg., is sensitive to 0·01 gram.

"Large volumes of gas are required in determining the tar by this method. Gases which contain much tar, and which are often still warm, are first passed through a long, weighed glass tube before they enter the absorption cylinder *A*. This tube slants toward *A* and is attached to *c*, and in it a sufficient cooling and condensation of the tar takes place. Most of the tar passes into *c* and collects at the bottom of *A*. 250 litres of gas are passed through the apparatus with a speed of from 30 to 40 litres an hour. If the gas to be examined has already passed through the condenser, or in other words, if the gas sample is taken either before or after the scrubbers, 500 litres of the gas must be used, and it may be given a speed of from 50 to 60 litres per hour.

"Operating in this manner, Tieftrunk found in every 1000 cubic metres of gas—

Before the condensers	.	150	to 200	kg. tar
„ scrubbers .	.	25	„ 75	„
After the scrubbers .	.	0·5	„ 20	„

"These figures are only approximate. They vary greatly, and the cause of these variations lies in the character of the coal, the method of distillation, the form of the condensers, the action of the same, the form and action of the scrubbers, the size of the apparatus, etc."

Bunsen [1] determines the gaseous hydrocarbons that are not properly gases, in purified illuminating gas, by slowly passing the gas, which is first carefully dried by calcium chloride, through a long glass tube bent slightly upward at its lower end, and then through a series of wash-bottles, the tube and wash-bottles being filled with absolute alcohol. The greater part of these liquid hydrocarbons which are present in the gas as vapours collect in the tube; only a very small amount is found in the alcohol of the last wash-bottle.

If the alcoholic contents of the washing apparatus be poured into a large excess of a concentrated solution of sodium chloride, the liquid hydrocarbons separate, without appreciable evolution of gas, as a milky cloud, which, upon standing, unites to a clear and colourless oily layer upon the surface of the salt solution. Three cubic metres of the Heidelberg illuminating gas, passed through one litre of alcohol, yielded a liquid which, after being freed from alcohol by washing with water and dried over calcium chloride, gave 36 grams of a clear liquid having the odour of pure benzene. This liquid began to boil between 80° and 90° C., and the boiling-point rose gradually to 140° C., only a very small residue boiling at a still higher temperature. By a number of fractional distillations the larger part of the total liquid was obtained as a product which boiled between 90° and 100° C., and which upon being cooled to below 0° C. separated almost completely as pure benzene.

The hydrocarbons taken up by alcohol consisted chiefly of benzene. The hydrocarbons mixed with the

[1] Bunsen, *Gasometrische Methoden*, 2d ed., p. 144.

benzene constituted so small a portion of the whole that their amounts could be wholly disregarded in the analysis as lying within the limits of experimental error.

In all of the illuminating gases, coming from the most varied sources, which Bunsen had opportunity to examine, not one contained less than from four to twelve times as much gas absorbable by sulphuric acid as there was benzene present. Hence that portion of illuminating gas which gives the lighting power consists chiefly of gaseous hydrocarbons.

The gases absorbable by sulphuric acid consist essentially of ethylene, propylene, and benzene vapours. All other hydrocarbons are here present in such small quantities that for analytical purposes they need not be considered.

If a more exhaustive analysis is to be made we must examine, in addition to those hydrocarbons absorbable by alcohol, those products also which result from leading large amounts of the gas through sulphuric acid, the products formed by the action of chlorine and bromine, the constituents separable by ammonium cuprous chloride, and finally, if possible, the condensation products which separate out when the gas is compressed.

E. St. Claire-Deville [1] has made a large number of determinations of these hydrocarbon vapours by separating them through cooling to $-22°$ C. We have tested this method and also that proposed by Bunsen (p. 221), and have obtained the following results:—[2]

1427 litres of illuminating gas gave by Bunsen's

[1] *Journal des usines à Gaz*, 1889, 13.

[2] Hempel and Dennis, *Berichte der deutsch. chem. Gesellschaft*, **24**, 1162.

method 15·4 ccm. of liquid hydrocarbons, from which, by fractional distillation and freezing, 3·5 ccm. of benzene was obtained.

1497 litres of illuminating gas gave by Deville's method 13 ccm. of liquid hydrocarbons, containing 5 ccm. benzene.

That the results by the two methods did not agree better is to be explained by the fact that it is almost impossible to keep the temperature constant at $-22°$ C. The experiments were made under the most favourable external conditions, *i.e.* during very cold days in winter, but in spite of the greatest care it was impossible to avoid considerable variations of temperature. More of the hydrocarbons were obtained by Bunsen's method than by that of Deville.

Further investigation showed that it is possible with 1 ccm. of alcohol to absorb and volumetrically determine the hydrocarbon vapour present in 100 ccm. of illuminating gas. These hydrocarbons are absorbed with 1 ccm. of alcohol, and the vapour of alcohol which has been taken up by the gas is removed by shaking the gas with 1 ccm. of water.

The alcohol and water are used in the explosion pipettes (Fig. 44). These explosion pipettes are first filled completely with mercury, and the alcohol and water are run in at *e* from burettes. Both liquids must be saturated with the illuminating gas before being used for the absorption. To do this, about 50 ccm. of illuminating gas is passed into each pipette, and the pipettes are shaken for several minutes. The gas is then driven out and the pipettes are ready for use.

The determination of the hydrocarbon vapours in the illuminating gas is made as follows:—

100 ccm. of the gas is measured off in a gas burette over thoroughly saturated confining water. The burette is joined by a fine-bore capillary to the pipette containing the 1 ccm. of alcohol, the gas is driven over, the pipette is closed by a pinchcock, and disconnected and shaken for three minutes. The gas is then drawn back into the burette and passed into the pipette containing the 1 ccm. of water, and is there shaken for three minutes. The gas is then drawn back into the pipette and measured. The measurement gives the amount of hydrocarbon vapours present.

Analyses of Dresden illuminating gas, made over mercury in the pipette shown in Fig. 19, gave—

0·74 per cent of hydrocarbon vapours
0·70 „ „ „

Measured over water in an ordinary gas burette, the results were—

0·5 per cent of hydrocarbon vapours
0·6 „ „ „

To prepare a gas containing a known amount of hydrocarbon vapours, 90 ccm. of the above gas was shaken for a short time with benzene contained in a gas pipette. The volume was hereby increased to 93·1 ccm. After the absorption of the hydrocarbon vapours, the residue was 89·4 ccm.

In a second experiment, 90 ccm. of the gas shaken with benzene increased to 93·0 ccm. After the absorption the volume was 89·4 ccm.

These experiments show that the method described admits of a volumetric and quantitatively exact determination of the hydrocarbon vapours.

Since these vapours are quite soluble in potassium hydroxide, their determination must precede those of the other constituents of the gas. Otherwise the results for carbon dioxide will be too high, and those for the heavy hydrocarbons too low.

Variations of temperature during the analysis should be avoided as far as possible, and great care must be taken that no alcohol enter the piece of rubber tubing which closes the burette.

4. *The Volumetric Analysis.*

For the volumetric analysis, a sufficient quantity of water must first be saturated with the illuminating gas, as directed on p. 39. The same must be done with the caustic potash pipette, unless a double pipette for solid and liquid reagents, which is filled with illuminating gas, is being used.

The hydrocarbon vapours are first absorbed with alcohol, then carbon dioxide with potassium hydroxide, then the heavy hydrocarbons with fuming sulphuric acid, then oxygen with phosphorus, and lastly carbon monoxide with the ammoniacal cuprous chloride solution. The residue, which consists of methane, hydrogen, and nitrogen, is measured, and is then led back into the cuprous chloride pipette, and a portion is taken for the explosion analysis.

With ordinary illuminating gas 12 ccm. of the residue suffice for the explosion.

These 12 ccm. are measured off in the gas burette, and enough air is drawn in to bring the mixture to about 100 ccm. In all these measurements the running down of the liquid must be most carefully waited

for, because the amount of gas taken is so small that any errors that may be made are greatly multiplied.

The gas mixture is now burned in the explosion pipette. The gas is then transferred to the burette and the total contraction is measured. Then the carbon dioxide is absorbed with potassium hydroxide, and finally the oxygen in excess is absorbed with phosphorus. The last determination is made merely to be sure that a sufficient excess of oxygen was present in the combustion.

An analysis of illuminating gas is here given for the sake of illustration.

100 ccm. of illuminating gas measured off (see p. 24).

Shaken with alcohol and then with water, as described on p. 224; drawn back into the burette and measured at the end of three minutes (time allowed for the running down).

0·7 ccm. or per cent hydrocarbon vapours.

Passed into caustic potash pipette and drawn directly back into the burette; measured after three minutes. Measurement gave 4·1 ccm.; hence there was present $4{\cdot}1 - 0{\cdot}7 = 3{\cdot}4$ ccm. or per cent carbon dioxide.

Burette now connected by means of a dry piece of rubber tube and a dry capillary with the pipette containing fuming sulphuric acid. Gas driven over and drawn back at once into the burette. Gas now passed again into caustic potash pipette, and after being drawn back into the burette and allowed to stand three minutes, again measured. The measurement gave 8·4 ccm.; hence there were $8{\cdot}4 - 4{\cdot}1 = 4{\cdot}3$ ccm. or 4·3 per cent of heavy hydrocarbons present.

The gas now passed into phosphorus pipette and

allowed to remain for three minutes; then drawn back into burette and measured at the end of three minutes. Reading gave 8·4 ccm.; hence no oxygen was present.

The gas was then passed into the pipette containing ammoniacal cuprous chloride which had been repeatedly used, and was shaken therein for two minutes. It was then drawn back into the burette and transferred at once to a second pipette containing ammoniacal cuprous chloride which had been used but little, and it was here shaken for three minutes. Drawn back into the burette and measured after three minutes; the reading was 18 ccm.; hence there was 18 ccm. — 8·4 = 9·6 ccm. or per cent carbon monoxide present.

The remaining 82 ccm. of gas was then passed back into the cuprous chloride pipette, and the pipette was closed with an ordinary pinchcock.

The water in the burette is poured out, the burette washed with hydrochloric acid and then with distilled water, and then filled with water which is saturated not with illuminating gas, but with air.

12 to 15 ccm. of the gas residue is now measured off into the burette. In this case 13·2 ccm. was taken.

So much air is then drawn in that the total volume of the gas residue taken and the air amounts to about 100 ccm. In this case it was 99·6 ccm.

This mixture is now brought into an explosion pipette filled with mercury, care being taken that the capillary remains full of water. The rubber connecting piece is closed by a strong pinchcock, and a piece of glass rod is slipped into the end of the rubber tube.

The pipette is then vigorously shaken, the glass stopcock is closed, the pipette is connected with the poles of an induction coil, and by lowering the dip battery the mixture is exploded. The glass stopcock is at once opened and the remaining gas is transferred without delay to the burette, and, after three minutes, measured. The result here was 78 ccm.

The total contraction was therefore $99{\cdot}6 - 78 = 21{\cdot}6$ ccm.

The gas remaining from the combustion is now passed into the caustic potash pipette, drawn directly back into the burette, and, after three minutes, measured. The reading was 73·2 ccm. Hence by the combustion $78 - 73{\cdot}2 = 4{\cdot}8$ ccm. of carbon dioxide was formed.

Although this gave all the data necessary for the calculation of the analysis, the remaining gas was nevertheless passed into the phosphorus pipette in order to be sure that an excess of oxygen was present in the combustion, or, in other words, that the gas was completely burned. The measurement gave 70·2 ccm.

Hence there was $73{\cdot}2 - 70{\cdot}2 = 3$ ccm. of oxygen in excess.

In the combustion of the marsh-gas its own volume of carbon dioxide is formed, so that in the 13·2 ccm. of the gas residue taken for the explosion there were 4·8 ccm. of marsh-gas.

The marsh-gas in the total gas residue of 82 ccm. is found by the proportion—

$$13{\cdot}2 : 82 = 4{\cdot}8 : x,$$
$$x = 29{\cdot}8 \text{ per cent marsh-gas.}$$

Since marsh-gas in burning unites with twice its volume of oxygen, the contraction which has resulted

from the combustion of the hydrogen is found by subtracting twice the volume of the carbon dioxide found from the total contraction. $21{\cdot}6 - (2 \times 4{\cdot}8) = 12$ ccm. contraction due to the burning of hydrogen.

One volume of hydrogen unites, in burning, with one-half its volume of oxygen; hence the volume of the hydrogen is found by multiplying 12 by $\frac{2}{3}$. Thus the 13·2 ccm. of the gas residue taken for the explosion contained 8 ccm. of hydrogen. The total amount of hydrogen is given by the proportion—

$$13{\cdot}2 : 82 = 8 : x,$$
$$x = 49{\cdot}6 \text{ per cent hydrogen.}$$

The nitrogen is found by subtracting the sum of all the other constituents from 100. This gives 2·6 per cent.

Hence the illuminating gas contained—

0·7	per cent	hydrocarbon vapours
3·4	„	carbon dioxide
4·3	„	heavy hydrocarbons
0·	„	oxygen
9·6	„	carbon monoxide
29·8	„	methane
49·6	„	hydrogen
2·6	„	nitrogen.
100·0		

In this analysis the following apparatus was used:—

One gas burette (Fig. 17, p. 22).

One gas pipette for fuming sulphuric acid (Fig. 60, p. 181).

Two double absorption pipettes for cuprous chloride (Fig. 22, p. 36).

A gas pipette for phosphorus (Fig. 21, p. 34).
An explosion pipette (Fig. 44, p. 103).
A small induction coil (Fig. 50, p. 110).
A dip battery (Fig. 49, p. 109).
A number of capillary connecting tubes.
A three-minute sand-glass.

With careful work, the determinations of the hydrocarbon vapours, carbon dioxide, heavy hydrocarbons, oxygen, and carbon monoxide are exact to about 0·2 per cent, but the experimental errors in the analysis of the marsh-gas, hydrogen, and nitrogen may rise to 1 per cent. The reason for this lies in the fact that only small quantities of gas can be taken for the explosion, and that all results are then calculated for a gas volume about six times as large. In the above example the proportion was 13·2 : 82.

It would be unadvisable, and would also lead to no greater accuracy, to explode very large volumes, because the error caused by the unequal heating of the gas mixture increases as the quantity of gas increases.

Direct comparison of two analyses, one of which was made entirely over mercury, while the other was carried out in a burette filled with water and an explosion pipette filled with mercury in the manner just described, showed that the determination of carbon dioxide by the latter method was quite exact.

As it was suspected that the residue of marsh-gas, hydrogen, and nitrogen might contain, in addition to these gases, higher members of the marsh-gas series, experiments were made to answer the question.

Mercury was employed as confining liquid and the greatest care was used. The result showed that

when the hydrogen had first been absorbed by palladium, the carbon dioxide formed in the explosion corresponded exactly to the oxygen used and the contraction observed. We may hence conclude that in ordinary illuminating gas there is no appreciable amount of ethane present with the methane.

The method of analysing illuminating gas described above is at the present time, in the author's opinion, the best and the most rapid.

The determination of hydrogen may be made more exactly by absorption with palladium (see p. 136). Yet many experiments have shown that the accuracy attained by making use of the fractional combustion of hydrogen is not greater than in the above procedure.

The following analysis is given to illustrate the calculation of the analysis when the hydrogen is fractionally burned.

The direct absorption gave—

0·6	per cent	hydrocarbon vapours
3·4	„	carbon dioxide
4·4	„	heavy hydrocarbons
0·3	„	oxygen
10·1	„	carbon monoxide.

The residue of hydrogen, methane, and nitrogen amounted to 81·2 ccm. This was transferred to a pipette and 40·5 ccm. were measured off in a burette for the fractional combustion of the hydrogen. To this was added air—in this case 58·7 ccm.—and the mixture was passed into a pipette filled with water. Then more air was measured off in the burette and transferred to the pipette, so that the total amount of

air added would without doubt be sufficient for the combustion of the hydrogen. In this second measurement 16·1 ccm. of air were taken, so that the total amount of gas taken for the fractional combustion was

$$40{\cdot}5 + 58{\cdot}7 + 16{\cdot}1 = 115{\cdot}3 \text{ ccm.}$$

The gases were vigorously shaken in the pipette to thoroughly mix them, and were then fractionally burned by leading them over 0·5 gram of palladium.

The volume after the combustion was 81 ccm.; hence the contraction was—

$$115{\cdot}3 - 81 = 34{\cdot}3 \text{ ccm.},$$

corresponding to 22·9 ccm. of hydrogen, the total amount of hydrogen being found by the proportion—

$$40{\cdot}5 : 81{\cdot}2 = 22{\cdot}9 : x,$$
$$x = 45{\cdot}9 \text{ per cent hydrogen.}$$

To determine the methane, 19·9 ccm. of the residue of hydrogen, methane, and nitrogen were taken and, together with 110 ccm. of air, were transferred to the explosion pipette. The gases were well mixed, and were then exploded, freed from carbon dioxide in the potassium hydroxide pipette, and measured. There remained 90·5 ccm. The contraction was—

$$110 + 19{\cdot}9 - 90{\cdot}5 = 39{\cdot}4 \text{ ccm.}$$

From the determination of the hydrogen by the fractional combustion we know that in 19·9 ccm. of the residue, the hydrogen would cause a contraction of

16·9 ccm. (40·5 : 19·9 = 34·3 : x, x = 16·9); hence the contraction due to the methane is equal to 39·4 — 16·9 = 22·5 ccm., and the volume of the methane itself is 7·5 ccm.

The per cent of methane is—

$$19{\cdot}9 : 81{\cdot}2 = 7{\cdot}5 : x,$$
$$x = 30{\cdot}6 \text{ per cent marsh-gas.}$$

The nitrogen determined by difference as before is 4·7 per cent, so that the composition of the gas was as follows :—

0·6	per cent	hydrocarbon vapours
3·4	„	carbon dioxide
4·4	„	heavy hydrocarbons
0·3	„	oxygen
10·1	„	carbon monoxide
45·9	„	hydrogen
30·6	„	marsh-gas
4·7	„	nitrogen.

Example to Illustrate the Method of Procedure and the Calculation in the Analysis of Generator Gas.

In addition to the apparatus used for the analysis of illuminating gas, a hydrogen pipette (p. 104) is here necessary.

The manipulation differs merely as concerns the combustion of the unabsorbable residue.

A generator gas made from brown coal in a shaft generator gave—

3·4	per cent	carbon dioxide
0·8	„	heavy hydrocarbons
0·3	„	oxygen
25·4	„	carbon monoxide.

The residue of marsh-gas, hydrogen, and nitrogen amounted to 70·1 ccm. The gas mixed with air would not explode, hence hydrogen was added.

The mixture that was exploded consisted of—

15·3 ccm. of the gas residue
84· „ air
10·5 „ hydrogen.

After the explosion the volume was

89·2 ccm.,

and the contraction was

$$(15{\cdot}3 + 84 + 10{\cdot}5) - 89{\cdot}2 = 20{\cdot}6 \text{ ccm.}$$

The 10·5 ccm. of hydrogen added, used up in its combustion 5·25 ccm. of oxygen, so that 15·75 ccm. must be subtracted from the total contraction to ascertain the contraction resulting from the hydrogen and marsh-gas in the generator gas.

This gives 4·85 ccm. contraction.

The absorption of the carbon dioxide formed in the combustion gave 1·3 ccm.

Since this volume is equal to that of the methane, the following proportion gives the per cent of the latter :—

$$15{\cdot}3 : 70{\cdot}1 = 1{\cdot}3 : x,$$
$$x = 5{\cdot}3 \text{ per cent marsh-gas.}$$

The marsh-gas unites with twice its volume of oxygen, so that the contraction resulting from the combustion of the hydrogen is found by subtracting twice the volume of the carbon dioxide formed from the total contraction—

$$4{\cdot}85 - (2 \times 1{\cdot}3) = 2{\cdot}25 \text{ ccm.}$$

Hence the 15·3 ccm. of the gas residue taken for the explosion contained—

$$2{\cdot}25 \times \tfrac{2}{3} = 1{\cdot}5 \text{ ccm. hydrogen,}$$

and the total amount of hydrogen is—

$$15{\cdot}3 : 70{\cdot}1 = 1{\cdot}5 : x,$$
$$x = 6{\cdot}8 \text{ ccm. or per cent hydrogen.}$$

The nitrogen, by difference, was 57·4 per cent. Hence the generator gas contained—

3·4	per cent	carbon dioxide
0·8	„	heavy hydrocarbons
0·3	„	oxygen
25·4	„	carbon monoxide
5·9	„	marsh-gas
6·8	„	hydrogen
57·4	„	nitrogen.

Berthelot's method for the analysis of illuminating gas, in which the heavy hydrocarbons are separated from benzene by bromine, and the benzene then absorbed by fuming nitric acid, has been found by F. P. Treadwell and H. N. Stokes[1] to be impracticable. On the one hand, bromine absorbs some benzene in addition to the ethylene, and, on the other hand, fuming nitric acid oxidises carbon monoxide. They found it possible to completely oxidise carbon monoxide by shaking the gas for a long time with fuming nitric acid.

The combustion of marsh-gas and hydrogen in gas mixtures can be effected without explosion by bringing the mixture in contact with a wire heated to redness by an electric current. J. Coquillion was the first to

[1] *Berichte der deutsch. chemischen Gesellschaft*, **21**, p. 3131.

devise a suitable apparatus therefor;[1] he named it a grisoumeter.

A short time ago this method was greatly improved by Cl. Winkler.[2] He uses a Hempel simple pipette for solid and liquid reagents (Fig. 67), and inserts into

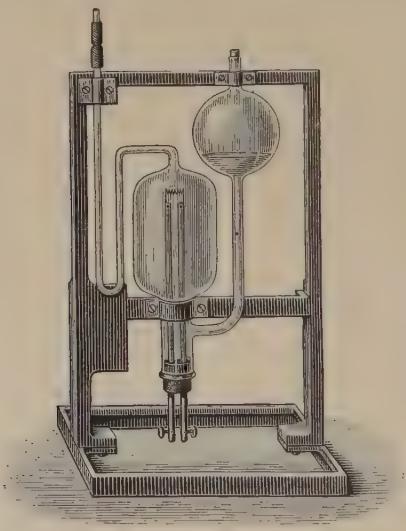

Fig. 67.

the neck a double-bore rubber stopper, through which pass two electrodes of lacquered brass about 175 mm. long and 5 mm. thick. At the lower ends of the rods are binding-screws for the wires from a battery, and the upper ends are joined by a spiral of platinum wire. This spiral is made of platinum wire 0·35 mm. thick, and is given the desired form by winding it about six times over a needle of 1·3 mm. diameter. The spiral

[1] Coquillion, *Compt. rendus*, 1877, vol. lxxxiv. p. 458.
[2] *Zeitschrift für analyt. Chemie*, **28**, pp. 269-289.

is held in place by small screws. To keep the electrodes in the proper position, the brass rods are passed through a double-bore cork, which is pushed up to about the middle of the cylindrical part of the pipette. (This cork is not shown in the figure.) The spiral should be from 2 to 2·5 cm. from the glass above it. The apparatus is filled with water. Winkler describes the manipulation as follows :—

"If the per cent of methane in a gas mixture, *e.g.* in illuminating gas, is to be determined with the aid of this apparatus, the carbon dioxide is first removed and determined by absorption with caustic potash, then the heavy hydrocarbons with fuming sulphuric acid, oxygen with alkaline pyrogallic acid solution, and carbon monoxide with ammoniacal cuprous chloride. The whole or a part of the remaining gas, consisting of hydrogen, methane, and nitrogen, is then mixed with an amount of oxygen more than sufficient to burn the hydrogen present, and the mixture is led over gently heated palladium asbestos. The hydrogen is thus burned and determined. The resulting contraction, divided by 3, gives the amount of oxygen which has united with the hydrogen and also the oxygen still remaining in the mixture. The volume of the air-nitrogen added is known, and the difference gives the volume of the unburned constituents of the gas. This last is regarded as pure methane, and so much air is now added that for 1 volume of methane there are at least 2 volumes of oxygen.

"The gas burette is now joined to the combustion pipette, which is wholly filled with water, the circuit is closed, and the gas is slowly driven over into the pipette. As soon as the gas has displaced the water

to such an extent that the spiral is exposed, the latter begins to glow brightly and the combustion proceeds quietly and without danger, if the remainder of the gas is slowly passed into the pipette. If the gas enters too rapidly, or if all of it be first brought into the pipette and the circuit then closed, a violent explosion may result, which will blow out the electrodes and the stoppers through the neck, and the confining water through the upper bulb. The thickness and length of the platinum wire and the number of turns given it must be adapted to the strength of the current. The figures given above are for a current which would be produced by two small Grove elements. If the wire is too fine, it melts off; if it is too thick, it does not become hot enough. The proper proportions are, however, easy to find.

"The combustion takes but little time, and is surely ended in one minute. The current is then interrupted, and the pipette, whose upper part has become quite warm, is allowed to cool somewhat. The gas is then passed back into the burette. The carbon dioxide is absorbed in the caustic potash pipette, and the gas is then measured. The observed contraction, divided by 3, gives the volume of the methane which was present."

The author prefers the method described on page 225, because, by means of the explosion, the combustion may be made in a moment, while with the combustion pipette the operation takes considerable time.

5. *The Determination of Sulphur.*

The sulphur in illuminating gas is present either

as hydrogen sulphide, or as carbon disulphide, or as some other combination with carbon and hydrogen.

Purified illuminating gas should be free from hydrogen sulphide. The hydrogen sulphide is determined by leading the gas through a suitable absorption apparatus containing a solution of lead nitrate. The resulting lead sulphide is filtered off, oxidised in a porcelain crucible with nitric acid, treated with a drop of sulphuric acid, evaporated to dryness, ignited, and weighed.

Bunte[1] determines the hydrogen sulphide in unpurified gas by measuring off 100 ccm. of the gas in one of the gas burettes devised by him, and then allowing a solution of iodine to enter until it is no longer decolorised—

$$H_2S + I_2 = S + 2HI.$$

The iodine solution is prepared by dissolving 1·134 grams of pure iodine in 1 litre of water. One ccm. of this solution corresponds to 0·1 ccm. of hydrogen sulphide at 0° and 760 mm. pressure. The sharpness of the reaction can be increased by adding starch-paste, the iodine being then added until the characteristic blue colour of the iodide of starch is seen.

Hydrogen sulphide can be separated from carbon dioxide by means of manganese dioxide, this substance holding back the hydrogen sulphide.

Carbon disulphide can be separated either as potassium xanthogenate, or as the tri-ethyl phosphorous compound.

A. Vogel has found[2] that the smallest amounts of

[1] Bunte, *Journal für Gasbeleuchtung*, 1888, **31**, 898.
[2] A. Vogel, *Annalen der Chemie und Pharm.*, 1853, 369.

carbon disulphide, when brought into a solution of potassium hydroxide in alcohol, form potassium xanthogenate—

$$CS_2 + KOH + C_2H_5OH = CS\begin{matrix}OC_2H_5\\SK\end{matrix} + H_2O.$$

To determine carbon disulphide, the gas is led through an alcoholic solution of potassium hydroxide, the alcohol is evaporated, acetic acid is added to slight acid reaction, and a dilute solution of cupric acetate is added. If carbon disulphide was present, a yellow precipitate results.

A. W. Hofmann has given [1] an exceptionally sharp reaction for carbon disulphide. If a gas containing traces of carbon disulphide be led through a suitable absorption apparatus containing a solution of tri-ethyl-phosphine in ether, the liquid turns red, and after the evaporation of the ether beautiful ruby-red crystals remain—

$$P(C_2H_5)_3 + CS_2 = P(C_2H_5)_3CS_2.$$

Since, however, a not inconsiderable portion of the sulphur in illuminating gas is present neither as hydrogen sulphide nor as carbon disulphide, a determination of the total sulphur of the gas is usually made.

After many experiments, the author is of the opinion that of the numerous methods which have been proposed for the determination of the total sulphur in illuminating gas, that of H. Drehschmidt is the best.

Drehschmidt describes the method as follows [2]:—

[1] A. W. Hofmann, *Ibid.*, **115**, 293.
[2] *Chemikerzeitung*, 1887, **11**, 1382.

"For some time I have used with good results the following method, which is similar to the English method and to that described by Poleck.[1] This method has an advantage over that of Valentin and Tieftrunk, which I formerly used exclusively, in that it does away with the necessity for an expensive platinum apparatus which called for frequent repairs. Moreover, the sulphur when determined by the latter method was usually 1·5 grams too low for every 100 cubic metres of gas.

"The illuminating gas under examination is measured in an experimental gas-meter which is supplied with a micrometer-screw, and passes thence through a glass tube to the Bunsen burner in the box *A*. The burner has a cap of wire-gauze to keep the flame from striking back, and is also fitted with the usual movable ring for regulating the supply of air. In the experiment this ring is brought into such a position that the flame is just made non-luminous. The tube *a* of the burner, into which the gas enters, passes through the side of the sheet-iron box and is soldered tightly in position. The glass tube coming from the meter is joined to *a* by a short piece of rubber tubing, the apparatus being thus movable to some extent. The box *A* consists of two parts, the upper being placed upon the lower and made tight by means of a conical joint. Into the lower part pass the branches of a fork-shaped tube through which the air for the combustion enters. This air first passes through *B*, which is filled with pieces of pumice-stone. A solution of potassium hydroxide or an alkaline lead solution is allowed to drop from the

[1] *Zeitschrift für analyt. Chemie*, 1883, **22**, p. 171; and *Chemiker-zeitung*, 1883, **7**, 519.

funnel upon the pumice-stone, and the air, thus freed from sulphur compounds, passes then through a rubber

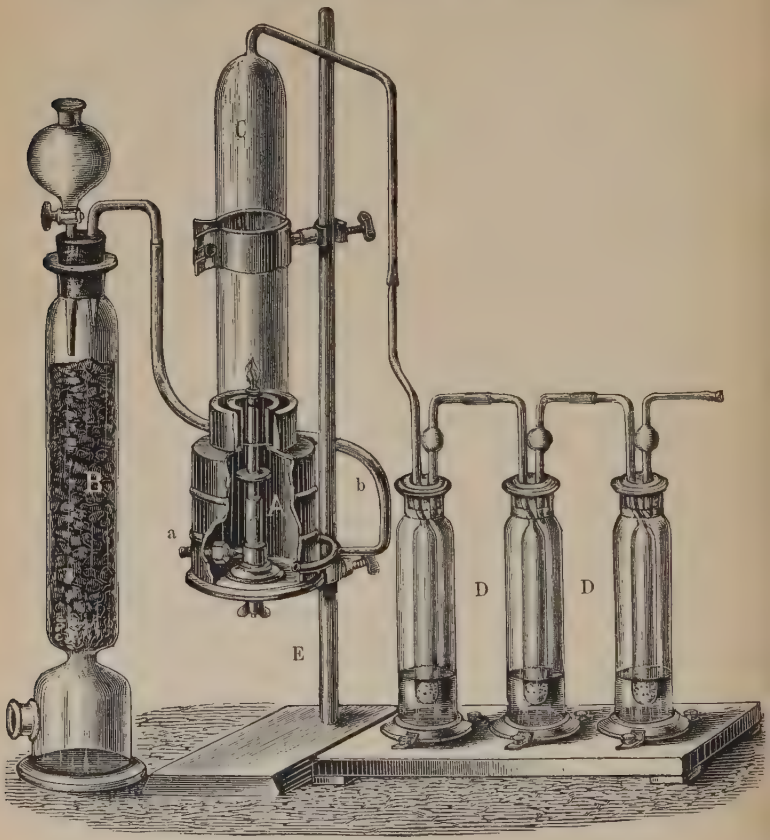

Fig. 68.

tube to *A*. The cover of the upper part of *A* has a circular opening above which the tube of the burner projects for some centimetres. The cover is double

walled, and the ring-shaped opening is partly filled with mercury, thus forming a mercury joint for the glass cylinder *C*. *C* is 5 cm. wide and 32 cm. long, and is supported by a broad ring-shaped band of brass, which is open on one side and is there supplied with a thumb-screw for drawing it together. The band is supplied at the back with the usual screw clamp. *C* ends in a glass tube which is bent downwards and connected to the tube from the absorption bottle *D* by a ground joint. The tube of the absorption bottle passes through the ground-glass stopper of the bottle and then widens to a cylinder which is closed at the bottom, but has, near the end, a row of small holes. The gas stream is finely divided by these small openings, and a rapid absorption of the sulphurous acid and sulphuric acid is thereby brought about. The gas passes from this bottle through a bulb tube into two other similar bottles. The connecting tubes of the three cylinders stand close together, and at the same height, and they are joined by short pieces of rubber tubing moistened with a little glycerin. The last of the absorption cylinders is connected with a water-jet aspirator by a piece of rubber tubing. The cylinders are fastened to a board by thumb-screws. The absorbing liquid used is a 5 per cent solution of potassium carbonate, 20 ccm. of the solution being put into each cylinder. In the first two cylinders a few drops of bromine are also added, to oxidise any sulphurous acid to sulphuric acid.

"In making a determination the three cylinders are filled in the manner described; they are then loosely fastened to the board, and the three inner cylinders, having previously been joined together, are lowered

into place. The meter is joined by the glass tube to *A*, the stand *E* being placed at the proper distance for permitting this. *C* is loosely fastened in the brass band, the board with the three cylinders is brought into such a position that the tube of the first cylinder will fit into the tube coming from *C*, and the brass band is then screwed tightly into position. The box *A*, while standing upon the table, is connected with the meter and the cylinder *B*, and the gas is lighted and allowed to burn at full height for two hours. The flame is then regulated to an hourly consumption of from 25 to 30 litres, and the aspirator is started. A reading of the meter is then made, and *A* is immediately raised so high that *C* dips into the mercury in the ring-shaped opening. The disc-shaped support upon which the box rests is then brought up under *A* and screwed tightly in position. The air-pump has an aspirating action upon the flame, and must hence be regulated. Whether enough air is drawn in may be told from the sharp contour which the flame shows when the supply of air is sufficient. The temperature of the measured illuminating gas is shown by a thermometer placed near the meter. 50 litres of gas are sufficient for an accurate sulphur determination. When the experiment is ended the apparatus is taken apart by lowering *A*, raising *C*, and removing the absorption cylinders from the board. *C* and the cylinders *D* are rinsed out into a beaker. The solution is acidified with hydrochloric acid, boiled until the bromine is driven off, and then precipitated with barium chloride. The sulphur found is calculated for 100 cbm. of gas at 10° C. and 760 mm. pressure. If 50 litres have been used for the determination, and if *t* denotes the

temperature of the gas, f the tension of aqueous vapour at this temperature, B the barometric pressure, and p the weight of the barium sulphate, then the amount of sulphur S in 100 cubic metres of the gas is—

$$S = 2000.p.0{\cdot}13748 \times \frac{750{\cdot}8}{283} \times \frac{273+t}{B-f} = p729{\cdot}47 \times \frac{273+t}{B-f}.$$

"The apparatus just described may be obtained from Dr. Rob. Muencke, Berlin, N.W."

6. *The Determination of Ammonia.*

Tieftrunk determines ammonia[1] by drawing the gas through a suitable absorption apparatus containing normal acid, and measuring the volume of gas with a meter.

If unwashed gas is being examined there is introduced between the meter and the absorption apparatus a tube filled with cotton, and a wash-bottle containing a solution of sugar of lead neutralised with acetic acid. These serve to hold back the hydrogen sulphide and the tar.

By titrating back the normal acid the amount of ammonia is found.

If the gas contains very much tar, the normal acid must be filtered before the titration. In this case a measured portion of the solution is taken for the titration, and the total ammonia is calculated therefrom.

[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II., p. 287.

7. *The Determination of Carbon Dioxide.*

The carbon dioxide can be determined with great

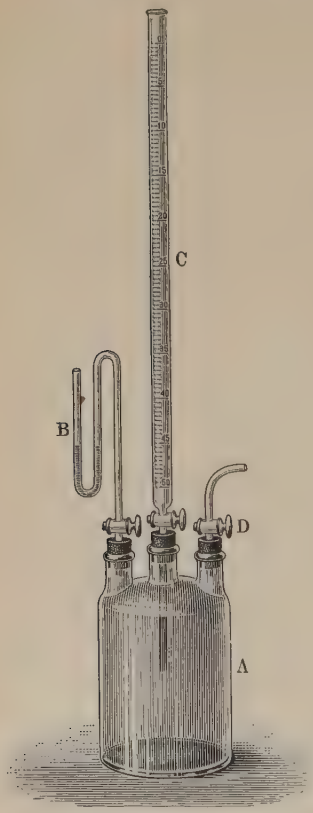

Fig. 69.

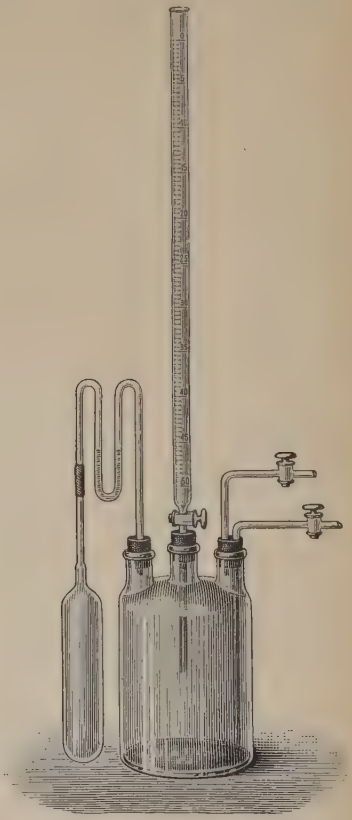

Fig. 70.

exactness with the apparatus devised by Rüdorff.[1]

[1] *Pogg. Annal.* vol. cxxv. p. 75. Also *Zeitschrift für analyt. Chemie*, 4, 231.

This consists of a three-necked bottle *A* (Fig. 69): in one neck the manometer *B*, filled with a solution of indigo, is inserted; in the second neck the glass stopcock pipette *C*, graduated in tenths; and in the third neck either a single glass stopcock or a double-bore stopper carrying two tubes, one of which reaches to the bottom of the bottle, while the other ends just below the stopper.

The exact contents of the bottle must be known. In making the determination, illuminating gas is led into the bottle until all of the air is driven out, the lighter gas being introduced at the top of the bottle and the heavier air passing out below. The stopcocks are now closed, and the manometer is brought to zero by carefully allowing some of the gas which is in the bottle, and which is under pressure, to escape. If now a solution of potassium hydroxide be allowed to drop from the pipette into the bottle, the carbon dioxide will be absorbed. The volume of the carbon dioxide present can be read off directly from the pipette, if, after the absorption, the manometer is again brought to zero by admitting more caustic potash.

In this determination the gas must of course be free from hydrogen sulphide. If this is not the case, the gas is passed through manganese dioxide before entering the apparatus. To avoid changes of temperature it is advisable to place the apparatus in a vessel of water during the experiment.

It is self-evident that the apparatus in this form is influenced by changes of temperature and pressure of the atmosphere. It can be made independent of these by attaching a Pettersson compensating tube to the manometer, as in Fig. 70.

CHAPTER III

GASES WHICH OCCUR IN THE MANUFACTURE OF SULPHURIC ACID

In the manufacture of sulphuric acid the gases are examined for—

1. Sulphur dioxide; it may also be desired here to determine at the same time the small amount of sulphur trioxide present.
2. Nitric oxide.
3. Nitrogen trioxide.
4. Oxygen.
5. Under certain circumstances an examination for nitrous oxide and nitrogen peroxide may also be desired.

1. *Sulphur Dioxide.*

In the manufacture of sulphuric acid the determination of the sulphur dioxide in the kiln-gases is of especial importance. Reich's method[1] has been universally adopted for this purpose. Reich's apparatus consists of a double-necked absorption

[1] F. Reich, *Berg- und Hüttenmänn. Zeitung*, 1858. Also Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II. pp. 118 and 353.

bottle *A*, the aspirator *B*, and the glass cylinder *E*. These are supported by a wooden stand as shown in Fig. 71. The rubber tube joining *A* and *B* is about 30 cm. long. *A* is half filled with water and 10 or 20 ccm. of a $\frac{1}{10}$ normal iodine solution are added. The aspirator *B* is filled with water.

Before making a determination, the air in the tubes leading to the apparatus is displaced by the gas to be examined. The apparatus is tight if, after a short time and as soon as the air in *A* is correspondingly expanded, the water ceases entirely to flow from the aspirator.

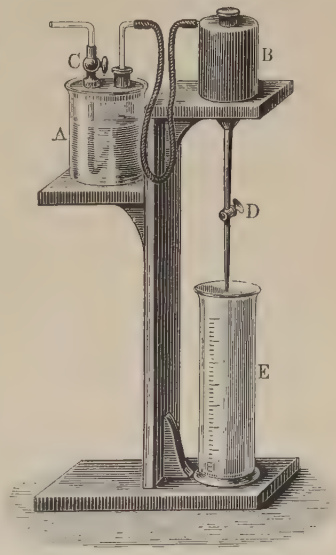

Fig. 71.

In making a determination the stop-cock *C* is opened, and the amount of water which is necessary to draw over sufficient gas to decolour the iodine solution, is measured in the cylinder *E*. During the experiment the bottle *A* is shaken. The volume of the water which has run out is equal to that of the gas taken, less the volume of the sulphur dioxide absorbed in *A*, and the quantity of sulphur dioxide present can be told from the amount of iodine used. Hence the per cent of sulphur dioxide present can be easily calculated. In accurate work the

variations of temperature and pressure must of course be taken into account.

When 10 ccm. of $\frac{1}{10}$ normal iodine solution are used all calculation may be avoided by using the following table, given by Lunge in his book on the Soda Manufacture :—

Water from Aspirator. Ccm.	Volume per cent of SO_2 in the Gas.
82	12·0
86	11·5
90	11·0
95	10·5
100	10·0
106	9·5
113	9·0
120	8·5
128	8·0
138	7·5
148	7·0
160	6·5
175	6·0
192	5·5
212	5·0

Provided that 6 per cent by volume of oxygen is present in the kiln-gases when they leave the lead-chamber, the gases should contain, according to Gerstenhöfer,[1] 10·65 per cent of sulphur dioxide when sulphur is burned, and 8·8 per cent when pyrites is roasted.

If considerable amounts of nitric oxide, nitrogen trioxide, nitrogen peroxide, or nitric acid, are mixed with the gases containing the sulphur dioxide, the

[1] Robert Hasenclever in A. W. Hofmann's *Bericht über d. Entwickelung d. chem. Industrie*, I. 170.

iodine method cannot be used, and it is best to determine the sulphur dioxide gravimetrically.

To determine sulphur trioxide in the presence of sulphur dioxide, the mixture of the two gases is led through a standardised solution of iodine;[1] the amount of the iodine acted upon by the sulphur dioxide is determined with sodium arsenite, and after acidifying with hydrochloric acid, the sulphuric acid is precipitated by barium chloride. Lunge and Salathe have shown that it is difficult to hold back sulphur trioxide with ordinary absorption apparatus. They have used with success the arrangement shown in Fig. 72. *A* is an ordinary bottle. The exit tube *b* is filled with glass beads, and at the lower end it is blown out to a bulb which is pierced with holes. The gas to be examined enters through *a*, passes through the liquid and then through the tube *b*. By sliding the tube *b* up and down, a position may easily be found in which the gas will carry along with it small amounts of the absorbing liquid, and will thus keep the glass beads constantly moistened with the reagent.

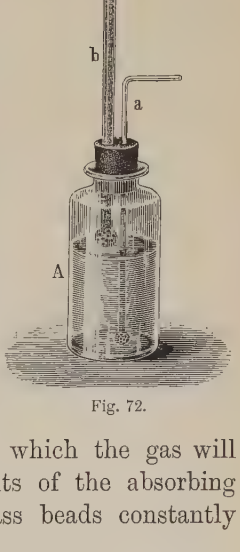

Fig. 72.

Lunge and Salathe used three such wash-bottles in determining the sulphur trioxide in kiln-gases.

[1] G. Lunge and F. Salathe, *Berichte der deutsch. chem. Ges.*, 1877, 1824.

chamber gases, all of the acid constituents are first removed by absorption with potassium hydroxide, and the oxygen is then absorbed with phosphorus, as suggested by Lindemann.

5. *Nitrous Oxide.*

Up to the present time nitrous oxide has not been detected with certainty in the gases of a sulphuric acid manufactory. It is, however, quite probable that this gas may be formed. Very small amounts cannot be determined, but when the quantity rises to about 0·3 per cent it can be determined by burning it with hydrogen in the explosion pipette, after all the absorbable gases have been removed. It must not be forgotten that nitrous oxide is very soluble in water, and that for this reason the absorbents must be carefully saturated with those gases which they do not absorb.

Nitrogen Peroxide.

In the manufacture of sulphuric acid the nitrogen peroxide which comes in question is always accompanied by nitrogen trioxide. According to Winkler and Lunge the nitrogen peroxide can be best determined by first absorbing the nitrogen peroxide and nitrogen trioxide together by concentrated sulphuric acid. A portion of the solution thus obtained is titrated with $\frac{N}{10}$ potassium permanganate, and in the other portion the gases are determined as nitric oxide in the nitrometer.

CHAPTER IV

THE ANALYSIS OF AIR

Up to the present time no direct method for determining nitrogen is known. Hence an analysis of the air calls for determinations of—

1. Aqueous vapour.
2. Carbon dioxide.
3. Carbon monoxide.
4. Oxygen.
5. Ozone.

For sanitary purposes, the determinations of carbon dioxide and water are those most frequently called for.

1. *The Determination of Aqueous Vapour in the Atmosphere.*

The water can be determined with great exactness by leading a measured or weighed volume of air through tubes filled with calcium chloride or phosphorus pentoxide, and ascertaining their increase in weight. It hardly need be mentioned that the calcium chloride must first be treated with carbon dioxide, so that it may contain no basic salt which, by taking up carbon dioxide, could change in weight.

The common phosphorus pentoxide is never pure, but always contains traces of phosphorus and phosphorous acid. For this reason, a current of dry air should be led for some time through the absorption apparatus before it is used.

Pettersson has devised an admirable apparatus with which the moisture and carbon dioxide of the atmosphere can be directly determined volumetrically. (See the determination of carbon dioxide in air, p. 267.)

For most purposes the hair hygrometer and the psychrometer give sufficiently accurate results.

A very fine form of the hair hygrometer devised by Saussure is made by Hermann Pfister, in Berne.

The construction of the instrument is based upon the property possessed by hair from which the oil has been removed, of lengthening or shortening according to the amount of moisture in the air. By alternately moistening and drying the hair thoroughly for a number of times, it is given, according to Pfister, the property of quite regular expansion.

Fig. 73 shows the arrangement. A hair, prepared as above mentioned, is fastened to a suitable frame. The hair passes around a little wheel below, and the changes in length cause the pointer to move and give the relative moisture directly on the scale.

August's psychrometer is based on the fact that water exposed to the air evaporates the more rapidly, and thereby extracts more heat from its surroundings, the farther the air is removed from the condition of saturation. From the lowering of the temperature $(t - t^1)$ of a thermometer which has been moistened in a suitable manner, the tension e of the water vapour in the air is calculated from the formula—

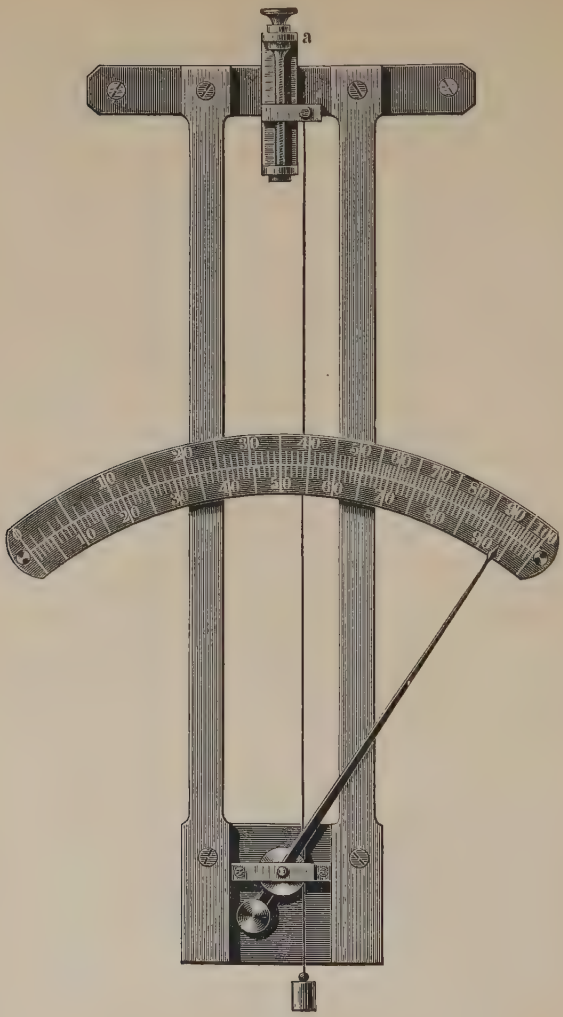

Fig. 73.

$$e = e^1 - k\,(t - t^1)\,b,$$

in which e^1 is the tension corresponding to the temperature t^1, b the barometric pressure in millimetres, and k an empirical factor which has, according to the researches of Regnault, the following values :—

In small closed rooms .	0·00128
„ large „ . .	0·00100
„ halls with open windows	0·00077
„ courts . . .	0·00074
„ open air (no wind) . .	0·00090

2. *The Determination of Carbon Dioxide in the Atmosphere.*

The most varied experience has shown that through the process of breathing, the air acquires properties which cause it to act deleteriously upon health when the products of breathing exceed a certain limit. Since we are not able by ordinary means to determine the other substances which are here formed, we make use of v. Pettenkofer's suggestion and judge of the purity of the air by the per cent of carbon dioxide present.

According to Pettenkofer the carbon dioxide in the air should not be raised, by breathing, to over 0·1 per cent.

The process best suited to the quantitative determination is that first used by Saussure and modified by Pettenkofer : it consists in absorbing the carbon dioxide of a measured volume of air with a barium hydroxide solution of known strength, and then determining, by titration with oxalic acid, the amount of barium hydroxide still unacted upon.

This method has been used by many investigators, and has been modified in minor details. A very practical form is that devised by W. Hesse.

Clemens Winkler[1] describes the method as follows:—

"W. Hesse's Method.[2]—This method is superior to the method of Pettenkofer, upon which it is based, in that it simplifies and shortens the determination of carbon dioxide, and can also be carried out at the place where the sample is taken, the possibility of employing it being thus much greater than formerly. By lessening the volume of the air to be examined, it became possible to diminish the size of the apparatus to portable form without limiting thereby the number of determinations.

"The necessary apparatus may be divided into a stationary and a portable portion.

"*A.* The reserve apparatus in the laboratory comprises the following:—

"1. A glass balloon or large bottle holding several litres, and filled with a concentrated solution of barium hydroxide. One kg. of barium hydroxide and 50 grams of barium chloride are put into from 4 to 5 kg. of distilled water. As the solution is used it is replaced by water as long as there is material in excess to saturate the water.

"2. A bottle containing dilute baryta water. The bottle is provided with a small absorption flask

[1] Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II. p. 375.

[2] Dr. W. Hesse, *Anleitung zur Bestimmung der Kohlensäure in der Luft, nebst einer Beschreibung des hierzu nöthigen Apparates;* Eulenberg's *Vierteljahrsschr. f. gerichtl. Medicin und öffentl. Sanitätswesen*, N.F. xxxi. 2.

containing pumice-stone saturated with caustic potash, for freeing the entering air from carbon dioxide (Fig. 74). This dilute baryta water is made by adding about 30 ccm. of concentrated barium hydroxide solution to 1 litre of water, or directly by dissolving 1·7 grams of a mixture of barium hydroxide and barium chloride (20 : 1) in 1 litre of distilled water.

"3. A solution of oxalic acid containing 5·6325

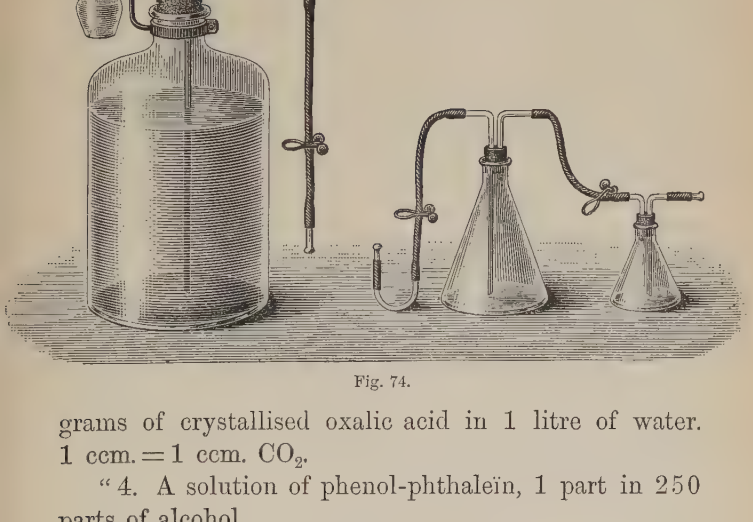

Fig. 74.

grams of crystallised oxalic acid in 1 litre of water. 1 ccm. = 1 ccm. CO_2.

"4. A solution of phenol-phthaleïn, 1 part in 250 parts of alcohol.

"*B.* The portable apparatus comprises—

"1. Five thick-walled conical Erlenmayer flasks of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{12}$, and $\frac{1}{16}$ litre capacity, and supplied with well fitting double-bore rubber stoppers. The point to which the rubber stopper reaches is marked on the first four flasks, and their capacity up to this mark is

written on the outside of each flask with a diamond. The openings of the stoppers of these four flasks are closed with pieces of glass rod from 3 to 5 cm. long. These rods are well rounded at the lower ends, the upper ends being widened like a button.

"2. A thick-walled 10 ccm. pipette.

"3. A glass stopcock burette holding from 10 to 15 ccm., graduated in tenths, and having a tip 7 to 10 cm. long.

"4. A 300 ccm. flask provided with a small guard bottle, as in *A* 2, and filled with dilute baryta water. This is filled in the laboratory by connecting it with the large reserve bottle containing dilute baryta water, and driving the solution over through the siphon. Before beginning the experiment a few drops of a solution of rosolic acid are added to the barium hydroxide solution. The fainter the colour the sharper is the reaction, but the colour must not be so faint as to be indistinct. The proper coloration will last for about three days; it is then so indistinct that a few drops of rosolic acid must again be added.

"5. A 250 ccm. bottle filled with dilute oxalic acid. This is prepared by bringing 25 ccm. of the standardised oxalic acid into the 250 ccm. flask, and then filling the flask to the mark with water.

"6. A thermometer.

"7. A barometer (a small aneroid).

"The amounts of solutions here given for the portable apparatus are sufficient for thirty separate determinations; in other words, at least ten analyses, including a control determination each time and the

standardising of the solution, can be made with the above quantities.

"Each determination of carbon dioxide by Hesse's method is a double one, the two determinations being made with volumes of air of different size. Accordingly, flasks of $\frac{1}{2}$ and $\frac{1}{4}$, or $\frac{1}{4}$ and $\frac{1}{8}$, or $\frac{1}{4}$ and $\frac{1}{12}$ litre capacity are used for taking the samples of air, the sizes of the flasks chosen depending upon whether a smaller or a larger amount of carbon dioxide in the air is to be expected. The samples are taken by completely filling the flasks at the place where the air is to be examined with water which has the temperature of the place, and then emptying the flasks and rinsing them with distilled water. In this operation care must be taken that the flask is not warmed by the hand, and that no air exhaled by the operator enters the flask.

"To absorb the carbon dioxide, the 10 ccm. pipette is put through one of the openings of a stopper fitting the flask, its end is inserted in the rubber tube of the supply flask, and the pipette is rinsed with a little barium hydroxide solution drawn up into it. The pipette is now filled to the zero mark by suction, and the stopper through which it passes is inserted in the neck of the flask containing the sample of air. The barium hydroxide is now run into the flask, the second opening of the stopper being obstructed with the finger or a glass rod to such an extent that the displaced air can just escape. The glass rod is then pushed into place, and the pipette is freed from the few drops of solution adhering to it by closing it at the top and warming it with the hand. The pipette is then drawn out of the stopper, and the second opening is closed with a glass rod. The same proceeding

is repeated with a second flask of different capacity. The two flasks are allowed to stand for some time with occasional shaking, and in the meantime the strength of the baryta water is determined.

The strength of the baryta water is determined by putting into the small flask of $\frac{1}{16}$ litre capacity nearly as much standardised oxalic acid solution as will be required in the titration, and then running in 10 ccm. of the solution of barium hydroxide. The solution is then neutralised by slowly running in more oxalic acid, and the total oxalic acid necessary is thus determined. By proceeding in this manner a very exact standardising of the solution is possible, even in an atmosphere containing much carbon dioxide, because the solution is never strongly alkaline enough to absorb appreciable amounts of carbon dioxide from the air.

"The baryta water which has been shaken with the air is titrated without previously removing the barium carbonate. The titration is made as follows:—

"Remove the glass rod from one of the openings in the stopper, and immediately insert the tip of the burette which has already been filled with oxalic acid solution. The tip of the burette should reach as far as possible into the flask (Fig. 75). Open the stop-cock of the burette and allow the oxalic acid to enter rapidly at first, but at the last only drop by drop. If the increased pressure resulting inside the flask checks the flow of liquid from the burette, this pressure is removed by lifting the glass stopper for a moment. When the solution is neutral, *i.e.* when it is completely decoloured, the height of the solution in the burette is noted, and the contents of the second flask is titrated in the same manner.

"It is clear that when the amount of carbon dioxide present is small, the accuracy of the determination is increased by using larger volumes of air. For this reason Hesse uses a flask of $\frac{3}{4}$ or 1 litre capacity whenever the carbon dioxide is probably below the limit for dwelling-rooms, as, for example, in the open air. He also uses these sizes when great accuracy is desired. Of course sufficient barium hydroxide solution must be taken to ensure its being present in excess up to the end of the operation. The small amount of carbon dioxide which the baryta water takes up from the air that it displaces when running into the flask may be disregarded.

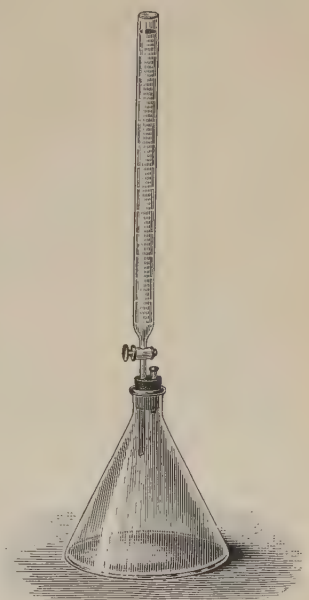

Fig. 75.

"In using this method for determining the carbon dioxide present in the soil or in walls, Hesse employs the apparatus shown in Fig. 76. The air in the soil is drawn through the flask by means of a rubber pump; the glass tubes are then removed, and the openings in the stopper are closed with glass rods. The titration is made as before described, but more concentrated reagents are required. In examining the air of graves, Hesse used a solution of barium

hydroxide ten times as strong as that previously given (10 ccm. = about 10 ccm. oxalic acid solution A3 = 10 ccm. CO_2).

"In calculating the analysis, the volume of air taken is reduced to normal pressure and temperature so that correct comparisons may be made. This calculation

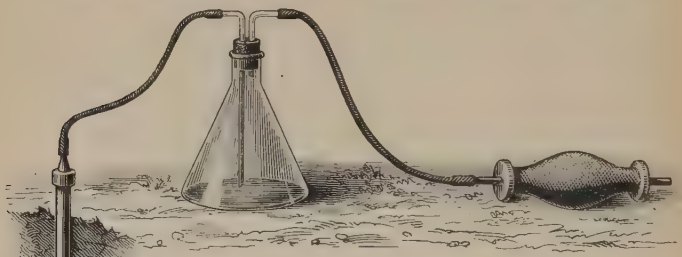

Fig. 76.

takes considerable time, and to Hesse belongs the merit of having compiled a table[1] giving the figures by which the amounts of carbon dioxide found in the uncorrected gas volume are to be multiplied. The table contains for each degree of temperature the multiplier for any barometric pressure.

"Example—

$$V = 223 \text{ ccm.}, t = 19°, b = 739 \text{ mm.};$$

the titration of the baryta water gave 10 ccm. baryta water = 11·5 ccm. oxalic acid, and in the experiment 6·2 ccm. oxalic acid was used. Hence the amount of carbon dioxide which had already

[1] Dr. med. Walter Hesse, *Tabellen zur Reduction eines Gasvolumes auf* 0° *Temperatur und* 760 *mm. Luftdruck.* Braunschweig, 1879.

united with the barium hydroxide was equivalent to $11{\cdot}5 - 6{\cdot}2 = 5{\cdot}3$ ccm. oxalic acid, corresponding to $0{\cdot}53$ ccm. CO_2, and we have the proportion—

$$[223 - 10]^1 \text{ or } 213 : 0{\cdot}53 = 1000 : x,$$

$$x = 2{\cdot}49 \text{ ccm. (in unreduced litre).}$$

"The multiplier corresponding to this temperature and barometric pressure is $1{\cdot}100$; hence in the reduced litre there are $2{\cdot}49 \times 1{\cdot}100 = 2{\cdot}7$ ccm., or in the air examined 2·7 parts per thousand of CO_2 present.

"The whole operation, including the control determination and the calculation, may be completed in from a quarter to half an hour. Hesse recommends that the results be put down in the form shown in the following table. The examples given show how well the results agree even under the most varied modifications. The calculations of the results given in the table[2] were made with the aid of logarithms, but are carried out to only one decimal."

[1] Subtraction from the volume to allow for the barium hydroxide solution which was run in.

[2] In the table—

h = time of day.
t = temperature centigrade.
b = barometric pressure in millimetres of mercury.
V = volume of glass flask.
BW = cubic centimetres of baryta water used.
Titer 9·35 means that 10 ccm. barium hydroxide solution = 9·35 ccm. oxalic acid = 0·935 ccm. CO_2.
Oxal. = cubic centimetres of oxalic acid solution used.
CO_2 unreduced = carbon dioxide in cubic centimetres in the unreduced litre.
CO_2 reduced = carbon dioxide in the reduced litre = parts per thousand.

Date.	Place.	Building.	Floor.	Number of persons in the room.	h	t	b	V	BW	Titer.	Oxal.	CO_2 unreduced.	Multiplier.	CO_2 reduced.	Remarks.
18.12.'78	Schwarzenberg	School	1st	68	3 P.M.	22	710·5	984	40	27·1	28·0	8·6	1·156	9·9	After a two-hour session.
								787	35		29·4	8·7		10·1	
								556	30		36·0	8·6		10·0	
								261	15		19·4	8·6		10·0	
								136	15		30·3	8·9		9·9	
4. 1.'79	,,	Bath	2d	3	8.30 P.M.	17	716·0	556	15	9·3	3·75	1·9	1·128	2·2	
								261	15		8·7	2·1		2·4	
								136	15		11·5	2·0		2·3	
5. 1.'79	,,	Outside atmosphere		...	12 M.	?	722·0	984	15	9·3	11·3	0·27	1·134	0·3	Titrated in a room at 21°.
								261	15		13·3	0·26		0·3	
19. 1.'79	,,	Bath	2d	1	8 A.M.	17	732·0	984	10	9·35	4·1	0·5	1·103	0·6	
								556	10		6·2	0·6		0·6	
								136	10		8·65	0·6		0·6	
27. 6.'79	Schneeberg	Apothecary's store	1st	2	2.45 P.M.	19	726·0	611	10	11·675	6·9	0·8	1·120	0·9	
								279	10		9·6	0·8		0·9	

PETTERSSON'S METHOD.

A very exact method for the determination of carbon dioxide and water vapour has been devised by Pettersson.[1] He describes the method as follows:—

"With the apparatus shown in Fig. 77 an accurate determination of the water and carbon dioxide in the air may be quickly made.

"*A* is a pipette with a graduated tube. It is joined at the top, by narrow but not capillary glass tubes, to the two reservoirs *B* and *C*. *B* is loosely filled with glass wool and phosphorus pentoxide, and *C* with glass wool and soda-lime. For the sake of clearness the connecting tubes are drawn in the figure much wider than they really are. The remainder of the apparatus, however, is shown so far as possible in the proper proportions. The whole system of the three glass reservoirs is immersed in a vessel of water in which the temperature is kept uniform, but of course not constant, by means of a stirrer. The handles of the stirrer are shown in Fig. 77 *r r*, and the disc in Fig. 78 *R*.

"The analysis consists in measuring a sample of air in the pipette *A*, then driving it over into the drying cylinder *B*, bringing it back into *A*, and measuring the decrease of volume caused by the drying. Then in similar manner the carbon dioxide present in the dried air is absorbed in *C*, and the decrease of volume is measured in *A*. The analysis thus comprises two different kinds of operations—

[1] *Zeitschrift für analytische Chemie*, **25**, pp. 467-484.

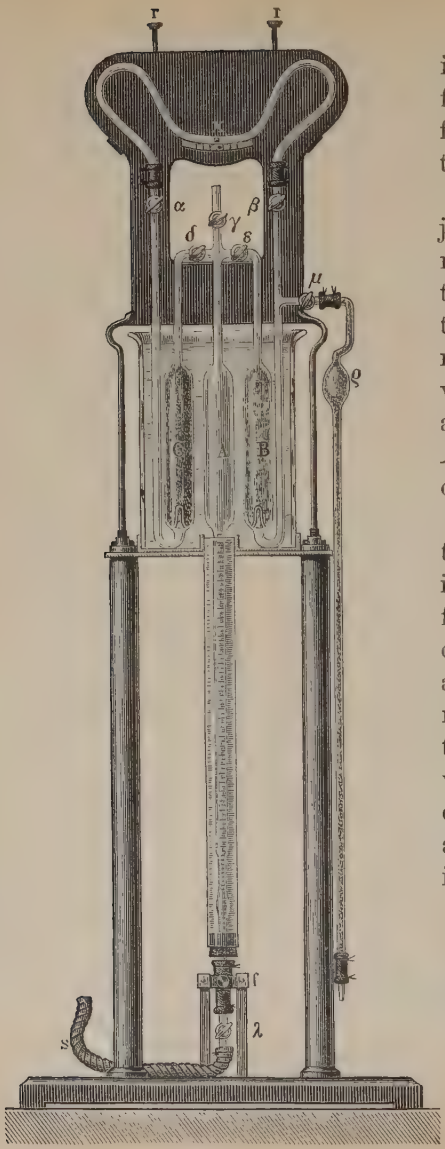

Fig. 77.

"1. The driving back and forth of the air from one vessel to another.

"2. The adjusting of the mercury level in the graduated tube, and the measuring of the volume of the air enclosed in *A* after each operation.

"1. The air to be examined is taken directly from the room or from the free atmosphere by means of a glass tube connected with the upper end of the pipette and passing out into the open

Fig. 78.

air. The pipette in the beginning is entirely filled with mercury, and the air is drawn in by allowing this mercury to run out until it stands about at the lower zero mark of the graduated tube. The stopcock λ is then closed, and the level of the mercury is accurately adjusted with the screw f, which, by means of a brass plate, compresses the rubber tube joining the stopcock λ with the graduated tube. If the level in the graduated tube has been brought at the beginning to nearly the proper position, a slight turning of the screw suffices for an accurate adjustment of the mercury. The adjustment may be made still sharper by using a magnifying glass. During this operation there is considerable pressure in the rubber tube upon which the screw acts. For this reason a piece of thick-walled rubber tubing is chosen, and, after it has been placed in position, an envelope of strong silk is sewed around it. The rubber will then hold for an unlimited time without bursting.

"When the pipette has been filled with air, δ, ϵ, α, and β are opened so that there may be the same pressure throughout the apparatus, and the stirrer is set in motion so that all parts of the apparatus may take the same temperature. The small drop of liquid x in the differential manometer will then come to rest opposite one of the marks on the little scale. This position must be accurately observed with the magnifier, because in all subsequent operations the drop must be brought to exactly the same position before a reading of the volumes is taken. After one is convinced that all differences of temperature and pressure

have been equalised, γ, δ, and β are closed. ϵ is left open. λ is now opened, and the mercury reservoir is raised by means of a sliding arrangement. The pipette *A* gradually fills with mercury, and the air is driven over into *B*. As *B* was full of dry air in the beginning, the pressure in it becomes quite high, and although in my apparatus the volume of *B* is about one-third larger than *A* (which contains exactly 100 ccm.), the movable mercury reservoir must be raised nearly 130 cm. in order to raise the mercury in the pipette from the lower zero mark to the ⊤ of the connecting tubes at the top, and thus drive all of the air in *A* over into *B*.

"As is well known, phosphorus pentoxide absorbs the moisture of the air rapidly and completely.[1] On that account it will perhaps be surprising that, according to my experience, the air entering *B* must be left for ten to twenty minutes in contact with the pentoxide in order to remove every trace of moisture. The result may be easily controlled by again passing the dried air into B, and then measuring the decrease in volume resulting from the second absorption. To be sure, the greater part of the moisture is absorbed in a few minutes, but the traces are removed from the air only after it has stood for some time in the drying cylinder *B*. The apparent difference between earlier experiments and my own experience concerning the rapidity with which phosphorus pentoxide completely absorbs moisture finds an easy explanation in the different conditions under which we operated. Up to the present time experimenters have determined

[1] See the work of Fresenius in *Zeitschrift f. analyt. Chemie*, **4**, 177. Also Dibbits, *ibid.* **15**, 121.

the rapidity with which a current of air passing over phosphorus pentoxide will lose the moisture which it contains. In my experiments a volume of air at rest is exposed to the dehydrating action of the pentoxide, and it is natural that a longer time should be necessary for the absorption to become complete.

"The absorption of the carbon dioxide in C is carried out in a similar manner. The stopcocks ϵ and α must be closed and δ opened: γ and μ remain closed during the whole analysis. The carbon dioxide is absorbed much more rapidly by the soda-lime than is the aqueous vapour by the phosphorus pentoxide. Ten minutes are usually sufficient for removing the last traces of the carbon dioxide, so that when the operation is repeated no further decrease in volume can be observed in the graduated tube. Since soda-lime loses one molecule of water for every molecule of carbon dioxide which it absorbs, I naturally expected that the air coming from C after having been freed from carbon dioxide would contain a slight amount of moisture, and that this moisture would have to be removed by repeated absorption in B. To my surprise, however, the air proved to be completely dry after the absorption of carbon dioxide, and although I passed the air into B after each determination of carbon dioxide, I was able to detect in only a few experiments a decrease of volume of about 0·003 or 0·004 per cent. This decrease was of course brought into the calculation, but it may have been accidental, since the average uncertainty in this determination of carbon dioxide amounts to about 0·002 per cent. I would here state that I use in C soda-lime which has been thoroughly

dried and heated, and that the quantity of carbon dioxide which is absorbed in each experiment (especially in the analyses of air from the streets of Stockholm, where the carbon dioxide amounts to only 0·039 to 0·059 per cent) is exceedingly small in comparison with the large amount of absorbent which certainly contains a great deal of lime. I have had the same experience with two different pieces of apparatus, yet I do not mean to assert that every soda-lime (a product which, as is known, is prepared in very different ways) would have the same action, or that the contents of the reservoir C in my apparatus will hold back the moisture as completely after several hundred analyses as it does now. It facilitates and shortens the analysis if the sample of air need be dried but once; and since it has turned out, although contrary to my expectation, that the moisture formed in the absorption of the carbon dioxide can be taken up completely by the soda-lime itself, I would advise that some quick-lime be mixed with the soda-lime. A few control experiments will of course best decide as to whether or not we can depend upon the dehydrating action of the soda-lime.

"2. I now come to the second kind of analytical operation, namely, the adjustment and the measuring of the gas volume. The principle of this new method permits the measuring of the volume of air, after each absorption, by a direct reading of the graduated tube without regard for any changes of temperature and pressure which may have taken place during the experiment. Variations in the pressure of the external atmosphere cannot affect the measurements, because the stopcocks γ and μ remain closed during the whole

analysis. The temperature of the water surrounding A, B, and C is kept uniform by stirring. To be sure, the temperature changes constantly, but the change is gradual, and the pressure in all three reservoirs, A, B, and C, rises or falls to the same extent. Two of these reservoirs are always in communication with each other; the third is, however, cut off from the others. For example, during the determination of water, A and B communicate through the stopcock ϵ, and of themselves form a distinct system; the air in C is separated from them from the beginning of the experiment by the closed stopcock δ. The operations above described are now carried out with the air in A, the air being passed into B, then brought back in dry condition into A, and the level of the confining mercury so adjusted by the eye that the air in A has approximately its original pressure. Upon now opening the stopcock β, the little index x in the differential manometer moves toward the right or left, according to whether the mercury in the graduated tube stands too low or too high. λ is closed and the screw f is turned until x has taken precisely the same position which it had at the beginning. It is obvious that the pressure in A and B is now identical with the pressure prevailing in C, because the air in C, the stopcock a being open, acts upon the left side of the drop of liquid x, and the slightest difference in pressure would cause a great displacement of the drop toward one side or the other. The sensitiveness is, in fact, so great that a very slight turning of f, which would increase or diminish the volume of air in A by 0·002 ccm., moves the index 1 mm. to the right or left. The nature of the drop of liquid x, which plays the part of an index, has a great

influence upon the size of the deviation. I prefer to use a drop of concentrated sulphuric acid coloured with indigo blue: the drop, in order to be easily movable, occupies only 3 to 4 mm. of the length of the manometer tube. The tube is slightly bent, so that the drop tends of itself to take a position in the middle. The width of the manometer tube has but little influence, provided that it is not too narrow. An index of high-boiling petroleum is even more sensitive than the sulphuric acid. Since the sensitiveness for slight differences of pressure is so great, the stopcocks β and α must be opened very carefully, to avoid driving the drop out of the manometer tube. It is best never to open both α and β at once, but to keep one stopcock closed until the level in the graduated tube has been brought into approximately correct adjustment. If the operation is thus carried out an analysis will never be lost.

"It follows from what has been said that the method in reality consists in bringing the sample of air after each operation under exactly the same relations of pressure and temperature as prevail in the second part of the system. For example, there is present in all parts of the apparatus at the beginning of the analysis a temperature t and a pressure p. During the absorption of the water the air in C is at rest and is separated from A and B. Its temperature changes gradually from t to t_1, the pressure from p to p_1. After the absorption of water, the dry air in A (and also that in B) is brought to the same pressure p_1 with the help of the screw f and the index x in the manner already described. The temperature is of course t_1. Hence the determination in the graduated tube of the

decrease in volume is made under another pressure and another temperature from those at the beginning. Nevertheless the decrease in volume gives directly and without correction the volume per cent of the moisture in the air, just as though the dried air were measured under constant temperature and constant pressure. It is easy to understand that if the temperature in the water jacket, and consequently in the whole apparatus, were brought back to t, the air would again have the original pressure p without any change whatever being necessary in the adjustment of the index or of the level of the mercury in the graduated tube. The glass vessels A and B on the one hand, and C on the other, as well as the air contained in them, change their volumes in the same proportion. Hence in this method the changes of temperature during the analysis eliminate themselves, and the determinations give directly (due regard being of course given to the table of calibration) the volume per cents of water and carbon dioxide.

" A few remarks may here be in place. The influence of variations of temperature upon the air volumes which are separated from each other—A and B from C in the determination of moisture, and in the carbon dioxide determination A and C from B—is reciprocally compensated by the uniform expansion of the glass vessels and the dry gases. If after the index has been brought to rest, the apparatus is left with the stopcocks α and β open and either δ or ϵ closed, the index does not move although the temperature of the water may slowly change several tenths of a degree. Only when the change of temperature amounts to whole degrees is there seen a tendency of the index to move

toward the right or left. This is caused by the unequal expansion of the solid phosphorus pentoxide in *B* and the soda-lime in *C*. The expansion of these substances is for the most part self-compensating, but it is never completely so, and the influence of this source of error is manifested, in experiments which last quite long, as a slight uncertainty amounting to some millionths of the total volume. This degree of accuracy has never been attained by any of the earlier methods for determining the moisture of the atmosphere, so that the slight uncertainty mentioned above may be wholly disregarded when the apparatus is used as a hygrometer. In the determination of the atmospheric carbon dioxide, however, it is desirable that this difficulty be removed. The defect in the compensation could be met by allowing some mercury to enter *B* or *C* until the expansion of the air in both was equal. I have not tried this expedient with my apparatus, because the following procedure accomplished the end.

Fig. 79.

"When the volume of the dried air has been measured in *A*, I do not proceed at once to the determination of carbon dioxide in the same volume of air. After the absorption of water the volume of the mercury usually stands in the wider part of the graduated tube (Fig. 79). Instead of making the reading after the carbon dioxide absorption upon the same portion of the scale, where 1 mm. = 0·01116 ccm., I prefer to open the stopcock μ and to allow a small volume of dry atmospheric air to enter *A* through *g* and *B* until the mercury again

stands at the lower zero mark of the graduated tube. Since the pipette with the graduated tube holds exactly 100 ccm., it now contains 100 ccm. of dry air under atmospheric pressure. γ, ϵ, a, and β are now opened for a couple of seconds to allow the air in C also to assume the pressure of the atmosphere. Then γ, a, ϵ, and μ are closed. δ is left open and the absorption of the carbon dioxide is brought about in ten minutes by driving the air from A into C. The decrease in volume is then measured in the lower narrow part of the graduated tube where 1 mm. = 0·00199 ccm. In such a short time (the determination of the carbon dioxide does not take half an hour) the temperature will not change enough to make the error in compensation amount to more than about 0·002 per cent. It is best, however, in determinations of atmospheric carbon dioxide which call for great exactness, to keep the temperature of the room relatively constant.[1] In analysing the air of rooms, where accuracy to the millionths need not be striven for, the work may be carried on in a newly heated room quite near the stove without any considerable errors resulting. One should, however, seek to avoid the action of direct radiation from a fire or from the sun. For the hygienic examination of the air of rooms, as well as for the hygrometric determination of the moisture of the atmosphere, where the accuracy demanded is not greater than 0·05 per cent, I have a small apparatus in which the pipette A holds only 18 ccm., the other

[1] Do not seek to obtain a constant temperature in the apparatus by pouring in warm or cold water. Every such addition is a source of sudden variations of temperature which make themselves known through the oscillations of the index. The index remains quiet only when the apparatus is left to itself.

parts of the apparatus being correspondingly small. This apparatus can be enclosed in a small wooden box 60 cm. high, and may be carried in the hand. Here also the absorption of the carbon dioxide is made with dry soda-lime, but the absorption of moisture is carried out in an Orsat tube filled with concentrated sulphuric acid. The compensation of the temperature variations is based upon the principle stated below. In this apparatus also the graduated tube has a wide and a narrow portion, but the wider part is *below* and serves for the determination of water, and the carbon dioxide determination is made in the narrow part of the tube which stands *above*.

"In working with the larger apparatus, one finds that the index does not at once come to rest after a determination of water or carbon dioxide has been made, and the mercury in the graduated tube properly adjusted. For from five to ten or twelve minutes the index slowly moves, giving the impression that in the pipette and the absorption vessel communicating with it—either *B* or *C*—the air *is being warmed*. This is actually the case. When the air which has been compressed in *B* or *C* enters *A* it expands *adiabatically* and becomes *cooler*.

"Only after several minutes' standing is this loss of heat equalised by the water outside the pipette. On this account the water must be stirred, and the reading must not be made until the index has come to rest. The analysis, which otherwise would take probably less than half an hour, is thus made considerably longer. For this reason, the absorption of water in the small apparatus for hygienic and hygrometric determinations is made in an Orsat tube fused on to the

apparatus, the adiabatic cooling being here imperceptible.

"When the water is absorbed by a solid substance it is indispensable that the vessel *B* be previously filled with the *same kind of dry air* as that to be analysed. *A* should not be filled with atmospheric air while *B* contains the dry air of the room, because, for reasons easily seen, the determination of the carbon dioxide would then be inexact. For this reason *B* is filled before the analysis with air of the same nature as that to be analysed later. This air enters *B* through the tube *g* containing phosphorus pentoxide and through the stopcock μ. The air is drawn in by first filling the pipette *A* with mercury, and then, having closed the stopcocks γ, δ, and β, lowering the mercury reservoir. The air enters *B* from below through a small projecting tube over which a ∩-shaped tube is placed, and takes the place of the air passing from *B* into *A*. The operation must of course be repeated several times, especially when samples of air from very different sources are successively analysed.

"Concerning the technical making of the apparatus the following may be said :—

"The three reservoirs *A*, *B*, and *C* form, with the connecting glass tubes, a single system. I order them from Franz Müller, in Bonn, Germany, who furnishes them at low prices and carefully made. I have preferred to have *A*, *B*, and *C* sent to me in separate pieces. I myself then fill *B* with phosphorus pentoxide and *C* with soda-lime, and also calibrate the graduated tube of the pipette *A*. The three reservoirs are then fastened with string in the proper position on a thin board. At the two places where the tubes are

to be fused together large holes are cut in the board, so that the ends of the glass tubes, which must be pushed close together, may be reached with the flame from all sides. After first warming them with an alcohol lamp, the glass tubes may be easily and tightly fused together with the help of a blast-lamp or a small gas blow-pipe. In this way it is easily possible without further practice to put together much more complicated pieces of glass apparatus. One might perhaps just as well order from the manufactory reservoirs which are already filled and joined together.

Fig. 80.

The ordinary Geissler stopcocks are usually made with sufficient care to enable them to withstand the pressure arising in the apparatus.[1] But since the slightest error makes the whole apparatus useless, Müller has made stopcocks of longer and less conical surface; these answer the purpose admirably. The tube connecting the glass stopcock λ with the movable mercury reservoir has to withstand a high internal pressure. For this purpose I use an ordinary rubber tube not too thin-walled—either red or black rubber is the best—and surround it with a spiral of flexible copper wire, as shown in Fig. 80. Such tubes are very easy to make, and they last for several years even when they have to withstand an internal pressure of more than one atmosphere. The glass connecting tubes and stopcocks should have openings not less than 1 mm. in diameter.

"The moisture in the atmosphere is usually determined with psychrometers and from the readings of

[1] *N.B.*—If they are not too conical in form.

the dry and wet thermometer,—the psychrometrical difference,—and with the help of empirically derived formulas and tables the result is expressed as the moisture pressure in millimetres of mercury. Since determinations of moisture can be easily and accurately carried out with my apparatus, I have made a number of parallel researches with psychrometer thermometers from the Central Meteorological Station. The agreement is generally good when the temperature of the air is not too low. In this case the psychrometric method, as is well known, cannot be used, because the differences become too minute or at times negative. On this account when scientific expeditions have spent the winter in arctic regions they have usually been obliged to give up the determination of the atmospheric moisture. I hope that in such cases, and generally in meteorological determinations of the moisture in the air, the apparatus described above, but of very much smaller dimensions, may do good service. The most natural and simple method for determining the moisture of the atmosphere is to directly ascertain the volume per cent of the aqueous gas or vapour without necessity of corrections for pressure or temperature. It is these corrections probably which deter chemists from using the other absorption methods for the determination of atmospheric moisture (Schwackhöfer's apparatus, etc.)

"The determination of the carbon dioxide in air is in itself so difficult that one must be prepared to use either relatively large apparatus or an inconvenient equipment and method of work. Instead of giving a résumé of the many methods and proposals in this line, I will call attention only to the experience of Professor

W. Spring in his well-known and admirable work upon the determination of the carbon dioxide in the air at Lüttich. Professor Spring carefully tested all of the methods in use, and the only method which he found good was the chemical determination of carbon dioxide with barium hydroxide ; the various volumetric methods could not be recommended because of the unfitness of *liquid* absorbents.

"For this reason I have used as absorbents *dry* phosphorus pentoxide and *dry* soda-lime, of which the former absorbs only water, the latter only carbon dioxide and water. As, however, I fully agree with Professor Spring that the chemical method (titration) is the most reliable of all the older methods, I have taken the trouble to obtain a series of parallel analyses by my method and by Pettenkofer's method in its latest improved form. Herr C. Sondén, Engineer and Chemist of the Hygienic Bureau in Stockholm, has been so kind as to make simultaneously with me, upon certain days in November and December 1885, determinations of the carbon dioxide in the air, using for the purpose large quantities (10 litres) of atmospheric air. The samples of air were taken on the balcony of the laboratory of the High School, which is quite centrally located in Stockholm.

"At the same time psychrometric determinations of the atmospheric moisture were made with the instruments from the Central Meteorological Station.

"As already stated the figures given by the psychrometer generally agree quite well with the analytical results ; a noticeable difference was seen only on the 9th of December, when the temperature of the air was rather low (below – 8° C.) A greater agreement

between the determinations of carbon dioxide by such different methods could hardly be expected.

Date.			Determinations of Water.	Determinations of Carbon Dioxide.		
Month.	Day.	Time.	Psychrometer.	Pettersson's Methods.		Pettenkofer's Method (Sondén).
			Per cent	Per cent	Per cent	Per cent
November	1	11·22	...	0·968	0·059	...
„	8	10·5	0·86	0·801	0·055	0·052
„	15	2·25	0·41	0·461	0·039	...
„	22	10·55	...	...	0·043	...
„	27	11·44	0·46	0·479	0·044	...
December	5	10·17	0·67	0·718	0·041	0·044
„	6	10·16	0·24	0·219	0·046	0·043
„	8	9·26	0·22	0·213	0·051	0·056
„	„	„	...	...	...	0·059
„	„	„	...	...	...	0·066
„	9	9·9	0·25	0·150	...	...

"From among the many analyses of the air of the laboratory, which in themselves are of but little interest, I will give some results obtained during the preceding week :—

May 6.	Moisture = 0·640 per cent.			Carbon dioxide =	...
„ 7.	„ = 0·687	„		„	= 0·134 per cent.
„ 8.	„ = 0·877	„		„	= 0·113 „
„ 9.	„ = 0·815	„		„	= 0·109 „
„ 10.	„ = 0·754	„		„	= ...

"I am endeavouring at the present time to apply the same analytical principle to the determination of oxygen in the atmosphere, and I hope later to be able to publish something on that subject."

For the determination of carbon dioxide, Otto Pettersson and A. Palmqvist have materially simplified the apparatus just described. They describe the new apparatus as follows :—

"Under the heading, 'The analysis of air upon a new principle,' published in the *Zeitschrift für analytische Chemie*, xxv. pp. 467 to 478, one of us has described an apparatus for volumetrically determining the amounts of moisture and carbon dioxide in the air directly, without corrections for variations of temperature and pressure. Since we desired to make use of this principle for the sanitary determination of carbon dioxide, which is made almost exclusively by the exact but rather complex and long method of Pettenkofer, we have endeavoured, with the co-operation of C. Sondén, to give to the apparatus described by Pettersson a simpler and more convenient form, and if possible to reduce the length of each determination from a half hour or more, down to a few minutes. This was accomplished by analysing the air not in an absolutely dry condition, but saturated with moisture. The complete drying of the air can be done only with phosphorus pentoxide, and this takes considerable time. When dry absorbents are used the absorption must take place under considerably increased pressure, a circumstance which calls for great care in the making of the apparatus, the construction of the glass stopcocks, the introduction of the absorbents, etc. In using moist air we must give up, it is true, the direct determination of the water vapour, but on the other hand it becomes possible to make a direct determination of the carbon dioxide by means of a liquid reagent, and the analysis is completed in a few minutes without the tubes being exposed to any appreciable increase of pressure.

"Fig. 81 shows the apparatus which we used, and which is easily portable. The apparatus can be

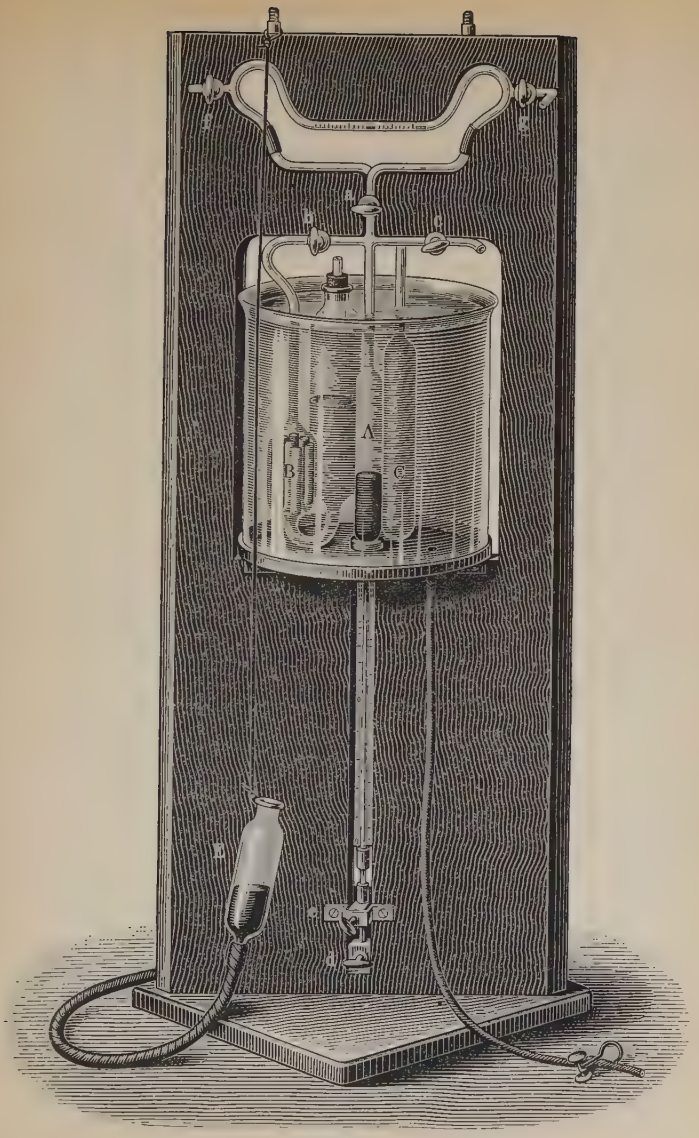

Fig. 81.

covered by a wooden box which fits over it, and to which a metal handle is strongly fastened (this cover is not shown in the figure). When the apparatus has been brought to the place where the air is to be examined, the glass jacket is filled with water, the outside air is drawn in through the tube *c*, and by a few simple manipulations, which take only a few minutes, the carbon dioxide is determined with an accuracy of about 0·01 per cent. The dimensions of the apparatus are as small as possible. For example, the pipette *A* into which the air to be analysed is drawn holds only about 18 ccm. With larger volumes of air it would be easy to attain greater accuracy.

"The carbon dioxide is absorbed in the Orsat potash-tube *B*, and the air is measured, before and after the absorption, in the pipette *A* and its graduated tube. The measuring pipette can be filled with mercury or air, or emptied of the same, by raising or lowering the mercury reservoir *E*, which is joined to the lower end of the graduated tube of *A* by means of a rubber tube wrapped with copper wire. There must always be a drop of water on the surface of the mercury; the air standing over the mercury is thus kept saturated with moisture. In reading the volumes, the meniscus of the mercury is each time so adjusted that the pressure in *A* is exactly the same as the pressure of the air in the compensation cylinder *C*.

"A differential manometer containing a drop of a coloured liquid (petroleum, in which azo-benzol is dissolved), and connected by capillary glass tubes on the one side with *A* and on the other with *C*, serves as the indicator in these operations. By moving the

reservoir *E* and then—having closed the stopcock *d*—suitably turning the screw *e*, the level of the mercury in *A* is so adjusted that the drop of liquid in the manometer stands at zero. It is obvious that in this manner it is always possible to bring back the air in *A* to the same pressure as that prevailing in the compensator *C*. Since the air in both the compensator and pipette is, from the beginning of the experiment, separated from the external atmosphere by closing the stopcocks *f*, *g*, and *c*, any variations in the external atmosphere have no effect. This is also true of changes in temperature; these eliminate themselves by acting in the same manner and to the same extent upon the tension of the air in *A* and *C*, provided that the water in the outer vessel which surrounds the main parts of the apparatus is sufficiently stirred. For these reasons no observation of temperature or barometric pressure is necessary. The changes in volume read off on the scale give directly the amount of carbon dioxide in hundredths of per cent by volume.

"Since the air is saturated with moisture before the absorption, it is clear that for strict correctness a slight correction is necessary to reduce the per cent of carbon dioxide found in the air saturated with moisture to the proper figure for the air in its actual condition. This simple correction is, however, of no importance because it is so small. An example will make this clear. It is evident that the correction is the larger the drier and warmer the air to be examined. Let us suppose that the temperature is 23° C., and that the air is so dry that it contains only 0·66 per cent of water vapour at a barometric pressure

of 760 mm. The difference between the dry and wet thermometer would then be 10° C., and the air when saturated with moisture would contain 2·68 per cent of water vapour. Let us suppose further that the air in the analysis, *i.e.* saturated with moisture, had shown a carbon dioxide per cent of 0·04. This air would contain 2·02 per cent more moisture than the atmosphere. The actual per cent of carbon dioxide then follows from the proportion—

$$100 : x = 97{\cdot}98 : 0{\cdot}04,$$
$$x = 0{\cdot}0408.$$

Hence the result given by the analysis was 0·0008 per cent too small.

"Each analysis consists of three operations.

"1. The air is drawn in from the outside and is measured, the level of the mercury in the graduated tube being brought to the zero mark. The upper and narrower part of the scale, where each division denotes $\frac{1}{10000}$ of the volume of the pipette, is used in analyses of atmospheric air, or the ordinary air of rooms, where the per cent of carbon dioxide is at the most not higher than 0·4 per cent. In the analysis of very impure air the lower part of the graduated tube is used, each division here corresponding to $\frac{1}{1000}$ of the whole volume. In measuring the volume the stopcocks *f*, *g*, *b*, *c* and *d* must be closed.

"2. The stopcocks *d* and *b* are opened, *a* is closed and the air is passed from *A* to *B*. After one or two minutes the carbon dioxide is absorbed and the air may be brought back into *A*, *b* is then closed and *a* is opened.

"3. The mercury level in *A* is so adjusted that the index again takes its normal position. The decrease in volume is then read off on the scale.

"The following table contains some parallel determinations which were simultaneously made with the same samples of air: (1) with the apparatus just described, (2) with a larger apparatus constructed upon the same principle by Sondén; and (3) by Pettenkofer's method. It is worthy of mention that in such parallel analyses, if they are to give results really exact to 0·01 per cent, the air must not be taken directly from the room, because the air of a room is not always homogeneous. The air samples must be taken from volumes of air confined in special reservoirs.

Series of Experiments.		Determination of Carbon Dioxide with the Portable Apparatus.	Determination of Carbon Dioxide with Sondén's Apparatus.	Determination of Carbon Dioxide by Pettenkofer's Method.
I.	a	0·03 per cent	0·041 per cent	...
	b	0·03 „	0·038 „	...
II.	a	0·46 „	0·463 „	...
	b	0·45 „	...	...
III.	a	0·195 „	0·211 „	0·22 per cent
	b	0·205 „	0·206 „	0·21 „
	c	0·21 „	0·210 „	...
IV.	a	0·23 „	0·227 „	0·23 „
	b	0·225 „	0·223 „	0·23 „
	c	0·22 „	...	...
V.	a	0·08 „	0·077 „	0·10 „
	b	0·07 „	...	0·09 „
VI.	a	0·17 „	0·170 „	...

"Any impurities in the measuring tube may be

easily removed by rinsing the pipette with water which is drawn in and driven out through *c*.

"We would in passing call attention to the fact that the Pettenkofer method can be very much shortened by closing the bottle in which the water is to be shaken with the barium hydroxide solution, not with a cap but with a tightly fitting perforated rubber stopper, through which is inserted a glass tube reaching to the bottom of the bottle. This glass tube has, at two or three different places, loosely inserted stoppers of pure cotton.

"After shaking the bottle, the glass tube can be connected with the branch tube of a glass stopcock burette, and the excess of barium hydroxide can be drawn up into the burette and immediately titrated.

"The baryta water may be somewhat cloudy after passing the first stopper of cotton, but it is filtered by the second and third, and enters the burette perfectly clear.

"Sulphur dioxide can also be titrated in the same way."

3. *Carbon Monoxide.*

On account of the very poisonous nature of carbon monoxide it is important in sanitary examinations of the air to determine the absence or presence of this gas. The blood reaction, which is fully described on page 165, is best adapted to this purpose.

4. *The Determination of Oxygen in the Atmosphere.*

The great significance which the oxygen in the atmosphere has for all living beings has made this

gas the subject of frequent investigations. Of the many methods which have been used for this purpose, two will be here described. One of these methods was in its fundamental principle thought out by von Jolly, and it has been brought by Kreusler to a very high degree of accuracy. The other method was used by the author in an examination of the air carried out in co-operation with Kreusler and Morley in 1886 and 1887. In this research Kreusler determined the oxygen by combustion with heated copper, Morley by combustion with hydrogen, and the author by absorbing it with potassium pyrogallate. By paying great care to all the necessary precautions, closely agreeing results were obtained by the three different methods.

The use of glowing metallic copper for the absorption excludes from its very nature all of those errors which may arise from the use of aqueous solutions, but much time is needed to carry it out. The method developed by the author, on the other hand, permits of rapid work, and by means of it the greatest accuracy can also be obtained if only due attention be given to the experimental details.

The apparatus used by U. Kreusler[1] (see Fig. 82) is described by him as follows:—

"A firm wooden stand *AA*, provided with set-screws, serves as a support for the barometer. The barometer consists of the long arm *BB* and the short arm *b* of equal diameter. They are joined together below by a strong rubber tube wrapped with linen. A similar and longer rubber tube connects the

[1] *Landwirthschaftliche Jahrbücher*, 1885, p. 333. See also Wiedemann's *Annalen der Physik und Chemie*, N. F. vol. vi. p. 520.

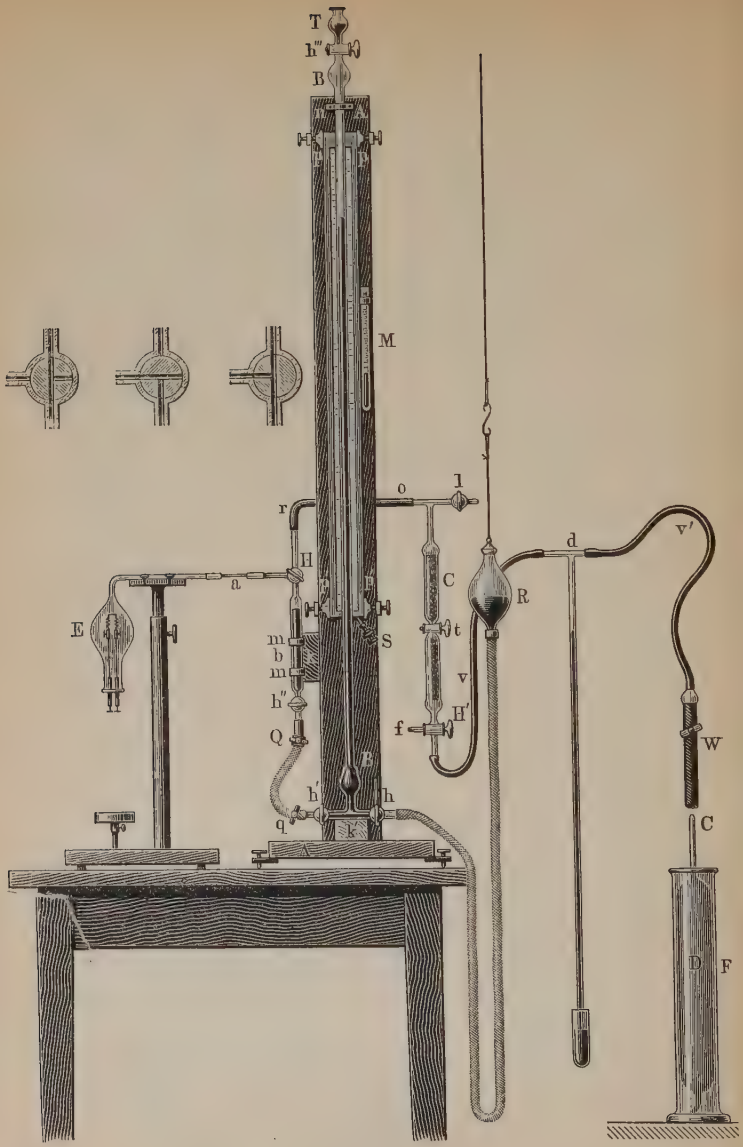

Fig. 82.

barometer with the movable reservoir of mercury *R*. The single bore glass stopcocks *h*, *h'* and *h''* permit of this communication being opened or closed as occasion demands. At the upper end, between the bulb of the tube *BB* and the funnel *T*, there is a fourth stopcock *h'''*, which is ground with especial care and is greased. On the capillary prolongation of *b* there is a three-way cock *H*, by means of which communication may be established through the tubes *a* and *ro* and the stopcock *l*, either between the arm *b* and the outside atmosphere (or air pump), or between *b* and the eudiometer *E*, or in both directions at once. (These positions are clearly shown in the enlarged drawing, p. 292.) Both arms of the barometer are fastened immovably to the wooden stand. *b* is held in place by means of the wooden block *k* and the tightly screwed metal bands *mm*. The cross-piece of *BB* rests upon a block *k'* and is fastened here and at the top at *n* with brass clamps. Between the tube and the board *A* of the stand there must be left a space sufficient for a strip of looking-glass, which is set in a brass frame. The glass is movable to a certain extent to permit of exact adjustment, and upon its surface a millimetre scale is etched. To facilitate the adjustment, the brass frame of the scale slides with slight friction between the guides *pp p'p'* ; these guides may be shifted to the right or left by means of the screws attached to them. The frame of the scale rests upon the rounded end of the set-screw *S*, which is provided with a check-nut. With this screw the scale may be moved up and down. By means of this arrangement the scale

can be easily brought into a perfectly perpendicular position, and any warping of the wooden support or any bend in the long glass tube is provided for: in addition, the adjustment of the zero mark of the scale can be easily improved at any time.

"The glass point fused into the upper part of the arm *b* serves as a limiting mark for the air that is to be examined, and as the beginning of the barometer graduation. The zero mark of the millimetre scale should lie in the same horizontal plane as the glass point. To make sure of this, the stopcocks *h'*, *h''* and *h'''* are opened, and the short arm is brought temporarily into communication with the outside air by suitably turning the three-way cock *H*. By raising the mercury reservoir *R* to the proper height by means of the cord which passes over a roller above, and by carefully opening the long-handled stopcock *h*, the two communicating arms of the barometer are slowly filled with mercury, the entrance of the mercury being stopped just before the mercury in *b* reaches the Jolly glass point. The final adjustment is more conveniently made with the help of the two Bunsen screw pinchcocks *Q* and *q*, *Q* being broad to give it greater effect. When the contact with the point has thus been brought about, the stopcock *h'* is closed to prevent any shaking of the rubber connecting tube from causing trouble. If the surface of the mercury in *B* does not now coincide with the zero mark of the scale behind it, the screw *S* is turned until this is effected, and is then fastened in position by screwing up the check-nut.

"Having thus made sure of the accuracy of the

zero mark's position, we proceed to the filling of the barometer. The instrument must of course be free from air. Clearing it by boiling is here impossible, and in fact quite unnecessary with a Torricellian vacuum of about 60 to 70 ccm., provided that all parts of the apparatus have been well cleaned and are dry. To thoroughly dry the apparatus I insert a calcium chloride tube into the mouth of *R* while the apparatus is still empty, close *h'*, open *h* and *h'''*, and draw air out through *T'* for quite a long time.[1] The rubber tube is then closed with a screw pinchcock close under the vessel *R*, and the system of tubes is exhausted as thoroughly as possible with a mercury air-pump attached at *T*. As soon as this is done the pinchcock of the reservoir *R*, which in the meantime has been filled with well-dried mercury, is gradually opened, and in this manner the rubber tube and the tube *B* are filled and at the same time kept free from bubbles of air. At the moment when the mercury enters the funnel *T'* (the reservoir must be raised if necessary) the stopcock *h'''* is closed. *h* is also closed and *h'* and *h''* are opened: a part of the mercury now passes into *b* producing a Torricellian vacuum in *BB*, and if *b* communicates through *H* with the outside atmosphere, the apparatus acts as an ordinary siphon barometer. A turn of the cock *H* changes the apparatus instantly into an equally delicate instrument that is completely independent of external variations in pressure, and which can be now used for measuring the pressure prevailing in the eudiometer *E*. To make the read-

[1] The arm *b* is dried in a similar manner.

ing, h' is closed and h is opened, and the vessel R is lowered until the mercury in BB stands somewhat lower than would correspond to the pressure to be expected. h is now closed and h' and h'' are carefully opened to see whether the above condition is fulfilled, or, in other words, whether the mercury does not tend to rise beyond the Jolly point. If it does, the column of mercury in the longer arm must of course be shortened. When all is in order R is again raised to the middle height, and h is opened for a moment to allow the mercury to rise nearly to the glass point. The delicate adjustment is made as already described with the pinchcocks Q and q,[1] which take the place of a micrometer screw.

"The reading on the mirror scale, which latter was devised by Jolly, may be made with extraordinary accuracy and sharpness after a little practice. According to my experience it is best to make the reading under artificial illumination. For this purpose I use a lantern covered with parchment paper. The lantern is so placed that the light always comes from the most favourable angle and from the height which will give the sharpest definition of the top of the mercury. It is then easily possible with the simplest form of telescope to read to tenths of a millimetre (the scale is divided into half-millimetres), and with a little practice 0·05 mm. may be read with certainty. Any

[1] After using, it is advisable to draw the mercury in b down again, so that it will not pass into the capillary if the pressure should by chance be lessened, and also that the glass may remain perfectly clean at the point where the readings are to be made.

According to my experience up to the present time, the vacuum of an instrument filled in this way and provided with the funnel at the top for preventing the entrance of air, holds as well as in any good barometer made on the ordinary plan.

error caused by parallax may be easily avoided, because the graduations are long enough to be clearly seen at the side of the real and reflected meniscus.

"The rest of the arrangement for carrying out an analysis of the air is not difficult to understand. The T-shaped tube *C* which is supported by a stand, not shown in the figure, serves to free the entering air from carbon dioxide and water vapour. Its lower part is filled with porous barium hydroxide, and the upper with pumice-stone saturated with sulphuric acid. The stopcock *t*, between the two, prevents the sulphuric acid from prematurely taking up water at the expense of the barium hydroxide, which absorbs carbon dioxide actively only when it contains a certain moderate amount of water. *H'* is a two-way glass stopcock. In the position shown in the figure it connects the drying tube with the adjoining tube *v*. The projection *f* is hollow, and, by turning the stopcock, the tubes either above or below it can be brought into communication with the outside air. The flexible tubes *v*, *v'*, and *w* connect the apparatus with the reservoir holding the sample of air. A barometer tube interposed at *d* enables one to judge of the rapidity with which the air enters, and, earlier, as to whether the exhausting of the apparatus is proceeding properly.

"It is most practicable to make the various parts of glass, and to connect them by ground-glass joints. Where flexibility is indispensable lead takes the place of glass, and in place of the ground-glass joints luting with sealing-wax is adopted. The connection with the eudiometer *E* must have a very small diameter, and hence a capillary steel tube *a* is used. The end

of the steel tube is carefully luted into a narrow ground-glass tube. The connecting pieces *ro*, *v*, and *v'* are of small lead tube, and at the only place where rubber could not well be avoided,[1] the short and thick-walled rubber tube *W* connecting the apparatus with the sample-holder is used.

Fig. 83.

"For collecting samples which are to be kept for a considerable time I use glass tubes which can be fused together (Fig. 83), instead of the bottles provided with stopcocks as proposed by Jolly. The projecting tube *d*, the walls of which must not be too thin, is drawn out to a fine point and fused together. The other tube is so contracted at two points, *b* and *c*, that later it may be easily melted together here. The tube is joined at *a* to the mercury air-pump and exhausted, and is then fused together at *b*. We are thus sure that the vacuum will remain up to the time for taking the air sample. The tube is filled with air by simply breaking off the tip at *b*. The end is then closed temporarily with wax or rubber, and the tube is melted together at *c* with the blow-pipe.

"To bring the sample into the eudiometer, the point *d* is broken off by striking it against the bottom of the tall cylinder *F* (Fig. 82) containing mercury. *D* is held down by a clamp attached to the edge of the

[1] Many experiments have convinced me that narrow and thick-walled (and especially paraffined) rubber tubes might be more extensively employed, for they remain sufficiently tight during the exhaustion if they are carefully wired on and luted. Only the necessity for frequent examination and occasional renewing caused me later to throw them aside and use the more durable metallic tubes.

cylinder. A file-mark is made near the end of *c*. The rubber tube *W* is slipped over *c*, and is well wired on, the ends being covered with sealing-wax. The tube at *l* is connected with the mercury air-pump, and all of the stopcocks excepting *h″* are so turned that free communication between all parts of the apparatus is established. The whole system is thus exhausted in one operation; on the one side the absorption tube *C*, etc., as far as the sample holder, and on the other side the manometer tube *b* and the eudiometer *E*. The eudiometer must of course previously be made ready by inserting the copper spiral.

"As soon as the desired degree of exhaustion has been reached, the stopcock *l* is at once closed, the clamp at *W* screwed together, and the tip *c* broken off inside the rubber tube surrounding it. Upon carefully opening the clamp and pouring mercury into *F* as needed, the air to be examined is slowly driven through the absorption tube *C* into the eudiometer. The fall of the mercury in the barometer tube *d* shows the rapidity of the operation and the pressure in the apparatus. When the filling is ended, *H* is so turned that the eudiometer communicates only with the manometer.

"*E* is now cooled with ice exactly as described by Jolly, and as soon as the gas ceases to contract, the level of the mercury is adjusted, and the reading is made as described above. After the wire has been heated (for this operation also the reader is referred to Jolly's work) and *E* again cooled with ice, communication is established between both arms of the barometer and the point-contact in *b* is again brought about. But it is obvious that before this is done the height of

the mercury in B must, with the help of the movable reservoir R, be decreased $\frac{1}{5}$ of its original amount. The quotient of the two readings gives directly the per cent of nitrogen, and consequently that of the oxygen also. A reduction for the temperature appears necessary only when that has changed considerably during the experiment. If the work be done in an unheated room and a screen be placed between the eudiometer and the barometer, the variations usually amount to only fractions of a degree, and the corresponding correction for the length of the mercury column seldom exceeds 0·1 mm. The thermometer M which is used is enclosed in a wide glass tube of the diameter of the barometer, and its bulb is surrounded with mercury. A thermometer whose bulb is free would of course change much more rapidly than the barometer.

"My first analyses with the Munich apparatus in the manner directed were not very satisfactory. However, for the sake of the deductions to be drawn from them, I think it best not to suppress these apparent failures, but to let the figures speak for themselves.[1]

"Samples of air of January 8th, 1883, 12 o'clock noon.

"Analysis No. 2.

"Samples from the bottle with stopcock—

20·458 per cent oxygen.

[1] Analysis No. 1 failed through premature melting-off of the copper wire, whose diameter, following Jolly's instructions, was only 0·5 mm. The use of a dynamo enabled me to subsequently use copper spirals of considerably thicker and longer wire, and to use each one of these for from two to three analyses, thus saving much time by avoiding the necessity of opening the apparatus each time.

"Analysis No. 3.

"Sample from the sealed cylinder—

20·740 per cent oxygen.

"The difference between the results and the lowness of No. 2 was later explained by the fact that in this experiment the dead space above the mercury in the manometer was not duly allowed for.

"Jolly's procedure in this detail is not clear from his paper. If the communication between the eudiometer and the manometer remains open, as it was at first, during the heating of the wire, then not only the air which in the beginning was in the capillary tube and upper part of the manometer, but also a considerable part of the air which was in the eudiometer itself, escapes for a time, because of its expansion, from the absorbent action of the copper. And even if this air is drawn back into the eudiometer each time by the intermittent cooling, the reaction cannot fail of being retarded under the above conditions.

"From this time on, my own procedure in this matter was as follows: During the heating I kept the rubber tube joining the manometer parts closed by a screw clamp (in the later apparatus, Fig. 82, the glass stopcock h'' answers the purpose still better), and at the moment when the circuit was broken I intentionally allowed the air to expand considerably. When the air cools it passes back into the eudiometer, and in this way the dead space is each time rinsed with air which has been in contact with the copper. The end of the operation is thus hastened considerably.

"Jolly states[1] that the end of the reaction may be told from the fact that the surface of the wire, which

[1] Letter to Professor Vogler (November 1882).

in the beginning is always being freshly oxidised, begins at last to melt. It is not clear whether a melting of the metal or of the layer of oxide is meant. The former would of course presuppose the maintenance of a temperature whose slightest increase would result in a breaking of the wire, and this could be seen only if the layer of oxide detached itself promptly during the cooling.

"With the wire that I used this was not wholly the case; but I noticed that the oxide, which at first was of a dull appearance, took on a somewhat fatty or glossy lustre as soon as it was further heated in an atmosphere free from oxygen. And after cooling it was no longer dull black, but, on the contrary, was a bright reddish brown, this colour resulting without doubt from the formation of cuprous oxide caused by the partial fusion of the black oxide with the metallic copper. It might seem as if this appearance could be taken as a sure sign of the end of the reaction, but the change of colour is not always sufficiently distinct; and for this reason I have later been satisfied with merely making throughout an ignition of a character and duration which many experiments have shown to be more than sufficient. After it had been found that for the given conditions a ten-minute heating of the wire repeated four times was sufficient, no less than six ten-minute heatings, and, when the wire was repeatedly used, no less than seven of these heatings were resorted to. It may also here be mentioned that an uninterrupted immersion of forty minutes in ice was found sufficient to cool the apparatus to 0°, but that in actual work the cooling always lasted sixty minutes at the least.

"Samples of air of January 10th, 12.30 P.M.

"Analysis No. 4.
"Sample from the bottle with stopcock, 1st half—

= 20·761 per cent oxygen.

"Analysis No. 5.
"Sample from the bottle with stopcock, 2d half—

= 20·587 per cent oxygen.

"Analysis No. 6.
"Sample from the sealed cylinder—

= 20·710 per cent oxygen.

"As there seemed at the time to be no other reason for these wholly inadmissible variations than that the heating was possibly still too weak and too short (the length of the heating had in no case, however, been less than fifty minutes), I thought that in the following experiments still greater attention would have to be given to this point.

"Samples of air of January 14th, 8 A.M.

"Analysis No. 7.
"From bottle with stopcock, 1st half. Heated nine times ten minutes each, at the end until the wire melted off = 20·575 per cent.

"Analysis No. 8.
"From bottle with stopcock, 2d half. Wire somewhat thicker; heated eight times ten minutes each, and at the end heated to a very bright glow—

= 20·574 per cent.

"Although these results are apparently very good, the figures, as will shortly be shown, are totally inaccurate, and the agreement is purely accidental.

"To be perfectly sure that all oxygen was absorbed and that the measurement was exact in every particular, I considered it necessary to carry on the heating still further with the same filling of the eudiometer, and to repeat the measurements after cooling the apparatus for different lengths of time.

"The results from No. 8 were now as follows:—

			Per cent.
a	Heated eight times, 10 minutes each time	Cooling with ice, 1 hr.	= 20·574
b	Further heated twice for 30 minutes	„ „ 1 „	= 20·486
c		„ „ 1½ „	= 20·491
d	Further heated six times, 10 minutes	„ „ 1 „	= 20·429
e		„ „ 2 hrs.	= 20·431
f		„ „ 7 „	= 20·466
g		„ „ 8 „	= 20·479

"The striking circumstance that, with repeated heating, the amount of oxygen constantly decreases, or, in other words, the pressure in the apparatus becomes greater, left no longer any doubt as to the presence of foreign substances, which tended to increase the pressure. The probability that water vapour was present was increased by the observation that, upon long standing, the pressure visibly decreased, perhaps in proportion as the copper oxide present absorbed more and more of the moisture.

"Although the entrance of moisture could not easily be explained, it appeared advisable to answer the question as to whether it was present by a direct experiment. For this purpose a piece of caustic

potash was placed in the eudiometer. Fortunately there still remained (in two sealed cylinders *A* and *B*) a supply of air from the samples already analysed.

"Analysis No. 9.

"Sample of air of January 14th, collected at the same time as the preceding sample, in the cylinder *A*, and analysed in the presence of caustic potash.

a	Wire heated nine times, 10 minutes each time	Cooling with ice	1 hour = 20·904 per cent.
b		,, ,,	2 hrs. = 20·918 ,,
c	Heated further four times, 15 minutes .	,, ,,	1 hour = 20·911 ,,

"Analysis No. 10.

"With cylinder *B*, exactly like the preceding.

a	Seven times, 10 minutes ;	cooling with ice	1 hour = 20·896 per cent.
b	Further, six times, 10 minutes . .	,, ,,	1 ,, = 20·892 ,,
c		,, ,,	2½ hrs. = 20·883 ,,

"We thus obtain from these experiments considerably higher and at the same time much better agreeing results. The greatest difference is—

With the same sample of air . . .	0·014 per cent.
With two different samples of the same air	0·035 ,,

"After making this observation, the correctness of which has been confirmed by many analyses (see those given later), I have never omitted to put a small stick of caustic potash into the eudiometer, the piece of caustic potash being placed in a small wire basket fastened in a suitable position. That the favourable action of the caustic potash was due to its absorption of water could not of course be as clearly seen from the appearance of this material as from that of the phosphorus pentoxide, which was used in most of the subsequent analyses. It was easy to see after every

experiment that the phosphorus pentoxide, which was placed in a little glass cup in the eudiometer, had deliquesced; the results, however, remained the same.[1]

"Before illustrating the correctness of the present method of procedure, I will call attention to some other precautions which, in my opinion, should be observed if the highest accuracy is to be attained.

"Instead of freeing the prepared spirals from fat, etc., by igniting them in the air, I now make the spirals of wire which has already been ignited, the layer of oxide being almost wholly removed by the winding of the wire. For the sake of the greatest possible accuracy, the spirals are again heated to glowing for a short time in the eudiometer, which has been previously made ready for an analysis and *exhausted*. Dry air is allowed to enter during the cooling, the apparatus is then exhausted a second time, and the air to be analysed is slowly admitted through the drying tube. In this way I have endeavoured—and, I think, with success—to reduce to a minimum the possibility of the existence of undesirable tensions.

"The determinations of pressure always represent

[1] Up to the present time I am able to give no definite information concerning the cause of the presence of the water. I consider it absolutely impossible that the moisture could have entered through the joints of the apparatus, or that—and this statement is confirmed by many different observations—the drying tube would allow such a large amount of water to pass through it. In my opinion, the method used for exhausting the apparatus offers the only explanation of the case. It seems obvious and unavoidable that, when the eudiometer is occasionally opened, moist air will enter and partially condense on the glass walls. When a vessel thus moistened is exhausted—especially when the air is pumped out rapidly—it is easy to conceive of a case in which the indicator of the pump will show a vacuum, while, in fact, there is still some water vapour in the receiver, the manometer not showing the presence of this moisture because the interposed drying apparatus stops it on the way.

the mean of several readings (usually 4 to 6), which were taken in rapid succession from the manometer and barometer alternately, when the original apparatus was used: this precaution, which was necessitated by the almost constant changing of the pressure of air, was, together with other intricacies, rendered unnecessary when the new apparatus was devised.

"When these rules are followed, there are scarcely any sources of error which need be feared. A leakage in the apparatus will be detected during the exhaustion, while any that might have arisen during the analysis will be shown by a distinctly abnormal result.

"Regarding this last point I may mention a case which to me was at first wholly unexplainable, and in which a considerable amount of air must have escaped from the apparatus, although the measurement of pressure before and after the heating showed that the instrument was air-tight. (The calculation would have given at least 30 per cent of oxygen!) The explanation was that the fat between the plate closing the eudiometer and the glass had been temporarily softened by becoming too warm, and had allowed some of the warm expanded air to pass through. After cooling, the contact closed again so completely that even the so-called optical contact appeared perfect, with the exception of one defect that was scarcely visible. When large spirals and dynamos are used, it is impossible to keep the eudiometer, and especially the pole-screws, from becoming quite warm; and to avoid the recurrence of the difficulty mentioned above, it has been found necessary to purposely cool the lower part of the eudiometer during the heating of the wire. The above example showed me that surrounding the

parts with ice would not protect them, because the ice would melt away, and the pole-screws, being left free, would heat up too much. So I immersed the neck of the eudiometer, together with the pole-screws and wires, in water, and since that time it has been impossible to detect the least defect in the optical contact.

"At the other joints, including the three-way cock, there is little danger of leakage if the work is well done, and if the proper attention is paid to these points.

"Although it was highly desirable that a large number of determinations in duplicate might be made, yet this could not be thought of because of the amount of time already consumed. Still I think that, as regards the chief results of the present research, this lack is of no great importance, for the results of the check determinations actually carried out may be assumed to assure to some extent the accuracy of the remaining analyses.

"I give in detail the analyses made with both forms of apparatus, for the reason that the results give the only sure basis for judging of the accuracy of the method.

"Although the two forms of apparatus were not directly compared with each other, the analyses show clearly that the results with the Munich apparatus are too low. Complete agreement between duplicate determinations was, however, obtained only after corrections had been introduced for a couple of slight inaccuracies in the scale of the Munich instrument as well as in the barometer. (In the results which follow these corrections are allowed for.) The scale of the later apparatus was compared with the standard scale of

the Poppelsdorf geodetic collection, and was found to be correct in all parts within the desired limits.

"A small error, which may be disregarded in relative determinations, is present in every case, for the oxygen, when absorbed by the copper, does not absolutely disappear, but on the contrary it causes an increase in the volume of the copper wire, and consequently a decrease in the space for the nitrogen, so that the pressure to be calculated to nitrogen comes out too high. The size of this error may easily be computed from the air-capacity of the eudiometer (250 ccm.), the amount of oxygen in the eudiometer when filled under average pressure (= 0·072 g.), and the increase in volume of the copper when a corresponding amount of the metal changes to cupric oxide (= 0·046).[1]

"Hence the error equals $\frac{0{\cdot}046}{250}$ or 0·00018 of the final volume of nitrogen, and consequently 0·00018 of the observed pressure, which must be corrected by this amount by subtracting it from the pressure read off. Although the results for the oxygen were changed on an average only + 0·01 per cent by the error, I saw no reason for not introducing this simple correction.

[1] A number of experiments upon this point, made by Dr. Dafert, showed that the copper oxide obtained from a large number of ignitions contained 85·92 per cent copper, and 14·08 per cent oxygen (corresponding to a mixture of 32·1 cupric oxide and 67·9 cuprous oxide). The specific gravity at 16° C. was 5·352, and that of the bright copper wire was 8·88. This gave all the necessary data for the above calculation.

"Further Experiments to show the Accuracy Attainable by the Copper Eudiometer.

"1. *With the Original Apparatus obtained from Munich.*

"Samples of air taken January 17th, 4 P.M.

Analysis No. 11.

Sample from the bottle with stopcock, 1st half.

		Per cent.
a	Wire heated 5 times, 10 minutes ; cooling with ice, 2½ hrs.	= 20·888
b	Wire heated further 4 times, 10 mins. ; ,, ,, 1 hr.	= 20·878

Analysis No. 12.

Sample from the bottle with stopcock, 2d half.

			Per cent.
a	The same wire heated 8 times, 10 minutes each	cooling with ice, 40 minutes	= 20·890
b		,, ,, 80 ,,	= 20·895

Analysis No. 13.

Sample from the sealed cylinder A.

	Per cent.
Fresh wire heated 65 minutes ; cooling with ice, 2½ hrs.	= 20·922

Analysis No. 14.

Sample from the sealed cylinder B.

	Per cent.
Previous wire heated 60 minutes ; cooling with ice, 52 min.	= 20·901

(Maximum differences between samples of the same air collected in different vessels = 0·044 per cent.)

"Samples of air taken January 26th, 8 A.M.

Analysis No. 15.

Sample from the bottle with stopcock, 1st half.

			Per cent.
a	Fresh wire heated 6 times, 10 minutes	cooling with ice, 50 mins.	= 20·920
b		,, ,, 3½ hours	= 20·935

Analysis No. 16.

Sample from the bottle with stopcock, 2d half.

			Per cent.
a *b*	Wire which had been used heated 7 times, 10 mins.	cooling with ice, 70 minutes	= 20·900
		,, ,, 105 ,,	= 20·905

(Maximum difference = 0·035 per cent.)

" 2. *Analysis with the new Poppelsdorf Apparatus.*

" Samples of air taken July 25th, 8.30 A.M.

Analysis No. 62.

Sample from the bottle with stopcock, 1st half.

			Per cent.
a	Fresh wire heated, 60 mins. ; cooling with ice, 100 mins.		= 20·930
b	Further heated 4 times, 10 minutes each	,, ,, 40 ,,	= 20·934
c		,, ,, 110 ,,	= 20·934

Analysis No. 63.

Sample from the bottle with stopcock, 2d half.

			Per cent.
a *b*	Wire which had been used heated 7 times, 10 mins.	cooling with ice, 95 minutes	= 20·916
		,, ,, 120 ,,	= 20·916

" Samples of air taken August 13th, 10 A.M.

Analysis No. 65.

Sample from bottle with stopcock A.

			Per cent.
a *b*	Fresh wire heated, 65 mins.	cooling with ice, 60 minutes	= 20·892
		,, ,, 80 ,,	= 20·893

Analysis No. 67.[1]

Sample from bottle with stopcock B, 1st half.

			Per cent.
a *b*	Fresh wire heated, 65 mins.	cooling with ice, 45 minutes	= 20·907
		,, ,, 55 ,,	= 20·909

Analysis No. 68.

Sample from bottle with stopcock B, 2d half.

		Per cent.
Used wire heated, 70 minutes ; cooling with ice, 60 minutes		= 20·886

[1] No. 66 was lost by leakage of the joint (see above).

"Samples of air taken October 18th, 3 P.M.

Analysis No. 69.

Sample from the bottle with stopcock, 1st third.

			Per cent.
a *b*	Fresh wire heated, 60 mins.	cooling with ice, 40 minutes	= 20·910
		,, ,, 55 ,,	= 20·917

Analysis No. 70.

Sample from the bottle with stopcock, 2d third.

			Per cent.
a *b*	Used wire heated, 60 mins.	cooling with ice, 31 minutes	= 20·904
		,, ,, 60 ,,	= 20·926

Analysis No. 71.

Sample from the bottle with stopcock, 3d third.

			Per cent.
a *b*	Wire which had been used twice, heated 80 minutes	cooling with ice, 40 minutes	= 20·917
		,, ,, 60 ,,	= 20·921

"As long as the cooling with ice does not fall below 40 minutes, very constant results are obtained, as shown in the following series :—

"Samples of air taken October 22d, 11.30 A.M.

Analysis No. 73.

Sample from the bottle with stopcock, 1st third.

			Per cent.
a *b*	Wire which had been once used, heated 75 minutes	cooling with ice, 60 minutes	= 20·905
		,, ,, 85 ,,	= 20·905

Analysis No. 74.

Sample from the bottle with stopcock, 2d third.

			Per cent.
a *b*	Fresh wire heated, 63 mins.	cooling with ice, 42 minutes	= 20·891
		,, ,, 71 ,,	= 20·893

Analysis No. 75.

Sample from the bottle with stopcock, 3d third.

			Per cent.
a *b*	Wire already used, heated 70 minutes	cooling with ice, 42 minutes	= 20·902
		,, ,, 63 ,,	= 20·899

"Samples of air taken October 25th, 10.30 A.M.

Analysis No. 79.

Sample from stopcock bottle A.

			Per cent.
a	Used wire heated, 70 mins.	cooling with ice, 47 minutes	= 20·916
b		,, ,, 62 ,,	= 20·915

Analysis No. 80.

Sample from stopcock bottle B.

			Per cent.
a	Fresh wire heated, 60 mins.	cooling with ice, 44 minutes	= 20·917
b		,, ,, 63 ,,	= 20·916

"As may be seen, the greatest differences in the preceding analyses—and these differences occur but once in each series of results—amount to—

For the Munich apparatus, 0·044 per cent.[1]
,, ,, Poppelsdorf ,, 0·023 per cent."

The Determination of Oxygen with the Apparatus for Exact Gas Analysis[2] (page 47).

The arrangement of the apparatus has already been described in detail, so that only a few particulars that are of importance in very accurate work will here be given.

The samples of air were collected in glass tubes which had been previously exhausted of air, as described on p. 6. The glass tubes were opened in a small mercury trough by breaking off the end of the tube with ordinary pliers. A small crucible was then

[1] Von Jolly at first found the limits of error to be somewhat less; later in a letter he states that they amount at the highest to 0·05 per cent.

[2] *Berichte der deutsch. chem. Gesellschaft*, 1885, p. 267; 1887, p. 1864.

slipped under the tube, and the tube was thus lifted out and put in a cylinder. The air was then drawn over into a gas pipette containing a very little water. This pipette was kept where it was somewhat warmer than the room in which the analysis was to be made. On days when the gas-laboratory had to be heated, the pipette stood near the heating-tube. In this simple manner the gas to be analysed was saturated with water, so that later it was not necessary to moisten

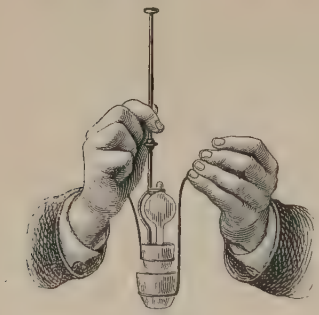

Fig. 84.

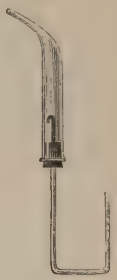

Fig. 85.

the measuring bulb. The measuring bulb was cleaned before each determination, and after being dried it was brought into the mercury-trough of the apparatus by placing it in two porcelain crucibles, one within the other (see Fig. 84), and filling these with mercury. If these are then lowered through the cooling water of the trough into the mercury, and the longer crucible removed by lowering it still further, the measuring bulb may now be lifted out of the small crucible under the surface of the mercury without a trace of water entering it. If only one crucible is used, water may easily get into the bulb, the probable cause being surface

adhesion. With the instrument shown in Fig. 85 the air was then sucked out of the measuring bulb and the gas sample was passed in from the gas pipette, great care being taken that no trace of water entered the bulb.

The readings of the pressure on the scale of the barometer tube were repeated every three minutes until there was no difference between two readings.

The pipette was filled with potassium pyrogallate, with the apparatus described on p. 118. After filling, the capillary of the pipette was placed in a beaker of water, and the capillary was freed from the reagent by carefully drawing in and driving out a little water.

When this washing was completed, as may be told with ease from the formation of the streaks in the water, the capillary of the pipette was placed in a beaker of fresh distilled water and a water-thread about 3 mm. long was drawn in. The capillary was then carefully dried on the outside. The gas was next drawn over into the pipette thus made ready, and the absorption of the oxygen was effected by shaking the pipette for five minutes. The advantage of the short thread of water in the capillary is that when the gas is drawn into the pipette the water once more rinses the capillary throughout its entire length.

After the absorption another short thread of water was drawn into the capillary by immersing the latter in distilled water, the pipette was then brought into position in the apparatus, and before driving the gas back into the measuring bulb mercury was sucked into the pipette through the capillary, the mercury driving the little thread of water before it. Upon blowing into the pipette the gas now passes into the measuring

bulb, being saturated with water vapour in its passage through the freshly moistened capillary.

It is thus easy to prevent any trace of the reagent from entering the measuring bulb. The agreement of the results is quite remarkable. The pipette must be frequently cleaned by drawing water into it so that muddy particles will not adhere to the glass.

An idea of the accuracy which can be attained by this method may be formed from the following figures.

In analyses of air samples kept in fused glass tubes my assistants, working more than a year apart, found—

	Oettel.	Schumann. (One year later.)
Air of April 14th, 1886.	20·89 per cent	20·89 per cent
Air of April 5th, 1886 .	20·93 „	20·94 „

In four analyses of the same sample Oettel found—

20·936 per cent	20·938 per cent
20·938 „	20·938 „

To permit of a comparison between the combustion method with copper and the absorption method with potassium pyrogallate, Herr Kreusler had the kindness to collect samples on three different days and to send them to Dresden. These samples were first analysed by my method by Herr Oettel in Dresden, and later by Herr Tacke and Herr Kreusler in Bonn. The results are given on p. 117.

Ozone.

For the detection and determination of ozone see p. 127.

CHAPTER V

THE DETERMINATION OF FLUORINE AS SILICON TETRAFLUORIDE.

At the suggestion of the author, O. W. F. Oettel has worked out the following method for the determination of fluorine. Oettel describes it as follows :—

"The method is based upon the decomposition of fluorine compounds by concentrated sulphuric acid in the presence of quartz, and the measurement of the evolved silicon tetrafluoride by displacement, in a manner quite similar to that in Scheibler's apparatus for the determination of carbon dioxide.

"The mercury, which is used as confining liquid, stands in a graduated burette, so that the displacement of the meniscus gives directly the volume of gas set free.

"The apparatus employed (Fig. 86), for which the author proposes the name Fluorometer, is made completely of glass, all rubber and cork connections which might cause error being avoided. The instrument consists of three parts : the evolution flask *A*, the graduated burette *B*, and the level-bulb *C*. The glass tube *a* of the small flask *A* is from 8 to 10 mm. wide. On one end of it is blown the bulb *b*, which holds 100 ccm.,

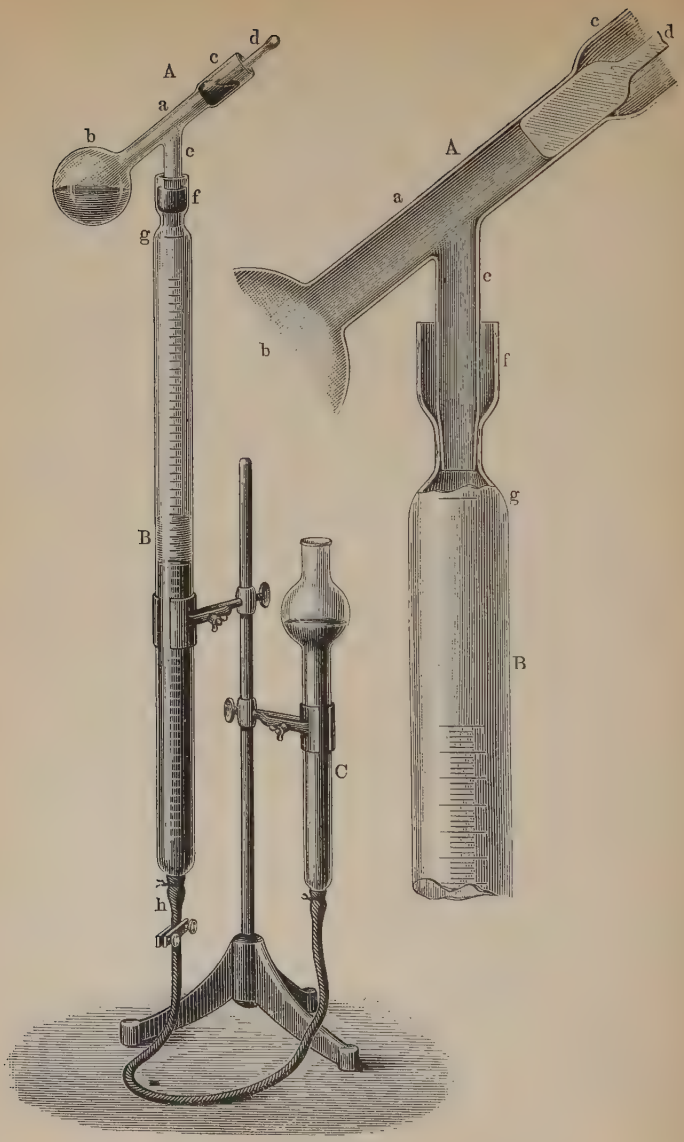

Fig. 86.

and at the other end it is widened into the bell *c* and closed with the ground-glass stopper *d*. Half way up *a*, the tube *e* is set on at an acute angle. The end of *e* is ground to fit into the upper end *f* of the burette *B*. There is a bell at *f* as at *c*; both of these serve to hold the mercury with which the two glass joints are covered during the experiment. As long as there is mercury in the bells a leakage at the joints is impossible, because the pressure in the apparatus is always somewhat less than the atmospheric pressure.

"The burette *B* has the length of a barometer, contains from 100 to 150 ccm., and is graduated in fifths of a cubic centimetre. Close under the bell *f* there is a mark *g*; the zero mark of the graduation is somewhat farther down. The part of the burette between these two marks contains from 7 to 10 ccm. The burette is joined at its lower end *h* with the level-bulb *C* by a thick-walled rubber tube fastened with wire ligatures. Instead of a thick-walled rubber tube two thin-walled tubes, one drawn over the other, may advantageously be used; greater freedom of movement is thus obtained.

"To make a determination of fluorine with this apparatus, proceed as follows:—

"Fill the burette to the zero mark with mercury by raising the level-bulb, close the connecting tube at *h* so that the level of the mercury cannot change, and pour in concentrated sulphuric acid up to the mark *g*. The finely powdered substance, well mixed with twenty times its amount of fine ignited quartz sand, has already been placed in the flask *A*. *A* is then set on the burette, mercury is poured into the bell *f* until the joint is covered, and the whole apparatus is allowed

to stand for a quarter of an hour, so that it may again assume the temperature of the room, which it may have lost by being touched with the hands. During this time the temperature, as shown by a thermometer hanging near the apparatus, is noted, and also the barometric pressure. When the fifteen minutes have passed, 50 ccm. of concentrated sulphuric acid are run into the flask *A* with a pipette, the stopper *d* is inserted, and the bell *c* is filled with mercury, exactly as was done with *f*. Until the stopper is put in place care must be taken not to warm *A* by touching it. The bulb *b* should be only half full, so that later the acid will not foam over into the burette.

"When the apparatus has thus been put together, the evolution of the silicon tetrafluoride is proceeded with. The screw-clamp *h* is removed, the air in *A* and the upper part of *B* being thus expanded. The bulb *b* is gradually heated with a small flame until the sulphuric acid begins to boil. As the gas is given off the mercury in *B* sinks, and the sulphuric acid above it covers the walls of the burette, and thus assures the absence of any trace of moisture. By adjusting the level-bulb a diminished pressure of from 10 to 15 cm. is kept in the apparatus. The contents of the flask is shaken from time to time by gently moving the whole stand. The bulb *b* is so heated that the sulphuric acid reaches its boiling-point in about twenty minutes; as soon as it begins to boil freely the decomposition is complete, the glass walls being slightly moistened, the acid ceasing to foam, and the quartz settling rapidly.

"The apparatus is now allowed to cool to the temperature of the room, this taking fully two hours. The

level-bulb *C* is raised from time to time to counterbalance the diminished pressure caused by the contraction of the gas.

"When the apparatus is completely cool the reading is made. The level-bulb is raised until the level of the mercury is the same as that in the burette, and the height of the mercury in the burette is read off. If the meniscus of the mercury at the beginning of the experiment stood exactly at the zero mark, the reading gives directly the volume of the evolved gas. The temperature of the room is noted, together with the height of the column of sulphuric acid standing above the mercury, for the pressure of this acid must be subtracted from the observed barometric pressure. With these data the volume of the silicon tetrafluoride given off is reduced to 0° C. and 760 mm. pressure. Usually neither the temperature nor the atmospheric pressure change during the experiment, but if they do the correction thus necessitated must be made not merely for the silicon tetrafluoride evolved, but for the total gas contained in the apparatus, SiF_4 + air.

"The volume of the air need be only approximately known, for the correction seldom amounts to more than a few tenths of a cubic centimetre.

"If the per cent of fluorine be thus directly calculated, the results are too low, because the concentrated sulphuric acid absorbs some silicon tetrafluoride. With the amount of acid given above, the average of several determinations gave the absorption as 1·4 ccm. (see the following analyses). This volume, 1·4 ccm., must be added to the reduced gas volume before calculating the per cent.

"1 ccm. SiF_4, at 0° C. and 76 mm. pressure, contains 3·4361 mg. fluorine (log = 0·53606).

"The concentrated sulphuric acid used in the work is made by heating the concentrated acid of the laboratory in a porcelain dish with flowers of sulphur. The acid is then poured off from the molten sulphur, and evaporated down to $\frac{2}{3}$ of its volume.

"The silicon dioxide required is best obtained by pulverising rock-crystal and igniting the powder in a combustion tube in a current of oxygen.

"To clean the apparatus, remove the flask *A* and insert in the end of *B* a cork carrying a siphon-shaped glass tube. The gas and sulphuric acid may then be easily driven out of the burette by raising the level-bulb *C*. The rubber tube is then closed at *h* to prevent the mercury from running back, and the burette is ready for the next determination. The flask is washed out with water and thoroughly dried.

"Analyses.

I.

CaF_2 taken, 0·4461 gram.
Temperature at the beginning, $t_1 = 21°$ C.
Temperature at the close, $t_2 = 21°$ C.
Barometric pressure, $B_1 = B_2 = 755·6$ mm.

The pressure of the column of sulphuric acid, expressed in millimetres of mercury, was $s = 5·4$ mm.

Hence the pressure of the gas $b = B - s = 750·2$ mm.
Observed volume of gas . . $V = 67·8$ ccm.
Reduced volume of gas . . $v = 62·13$ ccm.
Calculated . . . . . 63·25 ccm.
Difference = − 1·12 ccm. $SiF_4 = 3·8$ mg. F.

II.

CaF_2 taken, 0·4823 gram.
$t_1 = t_2 = 20{\cdot}5°$ C.
$B_1 = B_2 = 757{\cdot}0$ mm.
$s = 5{\cdot}4$ mm.
$b = 751{\cdot}6$ mm.
Observed volume of gas . $V = 72{\cdot}8$ ccm.
Reduced volume of gas . $v = 66{\cdot}96$ ccm.
Calculated . . . . 68·38 ccm.
Difference $= -1{\cdot}42$ ccm. $SiF_4 = 4{\cdot}8$ mg. F.

III.

CaF_2 taken, 0·2155 gram.
$t_1 = 20{\cdot}5°$, $t_2 = 20{\cdot}0°$.
$B_1 = B_2 = 759{\cdot}6$ mm.
$s = 5{\cdot}4$ mm.
$b = 754{\cdot}2$ mm.
Observed volume of gas . $V = 31{\cdot}5$ ccm.
Correction . . . $= +0{\cdot}14$ ccm.
Corrected volume . . $V_1 = 31{\cdot}64$ ccm.
Reduced volume of gas . $v = 29{\cdot}20$ ccm.
Calculated . . . . 30·55 ccm.
Difference $= -1{\cdot}35$ ccm. $SiF_4 = 4{\cdot}6$ mg. F.

IV.

CaF_2 taken, 0·5749 gram.
$t_1 = t_2 = 19{\cdot}7°$ C.
$B_1 = B_2 = 758{\cdot}5$ mm.
$s = 5{\cdot}4$ mm.
$b = 753{\cdot}1$ mm.
Observed volume of gas . $V = 86{\cdot}4$ ccm.
Reduced volume of gas . $v = 79{\cdot}85$ ccm.
Calculated . . . 81·51 ccm.
Difference $= -1{\cdot}66$ SiF_4 $= 5{\cdot}7$ mg. F.

V.

CaF_2 taken, 0·5710 gram.
$t_1 = 19·5°$, $t_2 = 19·0°$.
$B_1 = B_2 = 762·0$ mm.
$s = 5·4$ mm.
$b = 756·6$ mm.

Observed volume of gas .	$V =$	85·20 ccm.
Correction . . .	$=$	$+0·24$ ccm.
Corrected volume . .	$V_1 =$	85·44 ccm.
Reduced volume of gas .	$v =$	79·39 ccm.
Calculated		80·96 ccm.

Difference $= -1·57$ ccm. $SiF_4 = 5·4$ mg. F.

"The varying gas volumes, 30 to 80 ccm., obtained in the preceding experiments, show a fairly constant loss of from 1·12 to 1·66 ccm., corresponding to 3·8 to 5·7 mg. fluorine. The loss is explained if we assume that the sulphuric acid, of which the same amount was always used, absorbs the missing quantity of silicon tetrafluoride. The figures do not absolutely agree, because of the unavoidable experimental errors. If the correction + 1·4 ccm. is introduced into the calculations, the results for the fluorine are as follows :—

Found.	Calculated.	Found.	Calculated.
0·2183 g.	0·2173 g.	48·93 per cent	
0·2349 „	0·2350 „	48·70 „	
0·1051 „	0·1050 „	48·79 „	48·72 per cent.
0·2792 „	0·2801 „	48·56 „	
0·2776 „	0·2782 „	48·62 „	

"Petersen has more lately found the correction to be 1·7 ccm.

"This method is suited for the determination of fluorine in all substances, which are decomposed by

boiling concentrated sulphuric acid without giving off other gas than silicon tetrafluoride. Easily decomposable fluorides, which give off fluorine when sulphuric acid is poured over them, are enclosed in pieces of glass tubing. This is easily done by dipping one end of a short glass tube into molten primary potassium sulphate and allowing that to harden. The substance is then put in through the open end of the tube from a weighing tube, and this end is also closed with the sulphate. When the flask is heated the primary potassium sulphate melts, and the sulphuric acid comes in contact with the fluoride.

"The method is as accurate as that of Fresenius,[1] and is superior to his in being much quicker. A determination, including weighing and makings of the readings, takes about three hours; but the operator is engaged only a half hour of this time, the remaining interval being taken by the apparatus to assume the temperature of the room before and after the experiment.

"If there are a large number of analyses to be made, as may be the case in technical work, the determination may be made in an hour by placing the apparatus in cold water."

[1] *Zeitschrift für analyt. Chemie*, **5**, 190.

CHAPTER VI

APPARATUS FOR THE ANALYSIS OF SALTPETRE AND THE NITRIC ACID ESTERS (NITRO-GLYCERIN, GUN COTTON, ETC.)

WALTER CRUM[1] has found that the nitrogen acids dissolved in sulphuric acid (nitrogen trioxide, nitrogen peroxide, and nitric acid) are completely reduced to nitric oxide by shaking with mercury at ordinary temperatures. John Watts[2] and Georg Lunge[3] have worked out this method still further, and the latter has constructed an apparatus therefor which he calls a nitrometer. The author first[4] used the reaction for the decomposition of the nitric acid esters, and in particular for the determination of the nitro-glycerin in dynamite. Lunge has determined the conditions under which it is possible to analyse saltpetre in the same manner.

The above-mentioned analyses may be easily carried out in the apparatus here described (Fig. 87).

The apparatus consists of the evolution cylinder *c*, the level-bulb *e*, and the gas burette *ab*. *c* has at the top a glass stopcock *i*, and near the bottom a side tube *x*.

[1] *Ann. d. Chem. u. Pharm.* **62**, 233. Also *Jour. f. prakt. Chemie*, **41**, 201.
[2] *Chemical News*, **37**, 45.
[3] *Berichte der deutsch. chem. Gesellschaft*, **11**, 434.
[4] *Zeitschrift für analyt. Chemie*, **20**, 82.

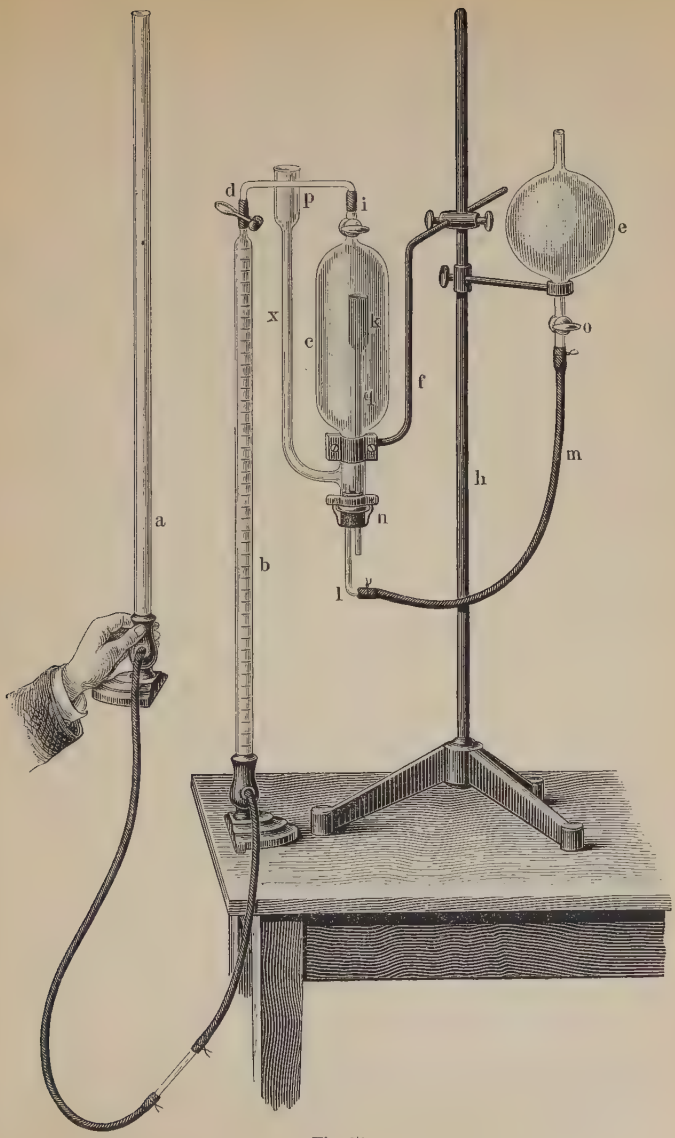

Fig. 87.

It is closed by a double-bore rubber stopper, over which passes a metallic band to keep it from being forced out by the pressure of the mercury. The long handle of the weighing-tube *k* passes through one opening of the stopper, and through the other is inserted the bent tube *l*, which is joined to the level-bulb *e* by the rubber tube *m*. The bulb *e* is supplied with a glass stopcock *o*.

To use this apparatus for the evaluation of dynamite or other nitric acid ester, fill the bulb *c* completely with mercury, *o* being closed; insert *k*, containing the weighed substance, in the rubber stopper, and put the apparatus together as shown in Fig. 87. The gas burette, however, is not yet connected with *i*. By opening *o* and *i* and raising *e*, *c* is completely filled with mercury. The stopcock *i* is then closed. If now the sulphuric acid required for the decomposition be poured into *x*, the acid may easily be brought into *c* by lowering the bulb *e*. The entrance of the sulphuric acid can be stopped at any moment by closing the stopcock *o*, and the introduction of air may be very easily avoided.

Atmospheric pressure is then re-established in the apparatus by raising *e* and opening *o*, and *c* is shaken until, with stopcock *o* closed, no rise of mercury can be observed in *x* after renewed shaking.

When, with *o* closed, the mercury in *x* remains at the same height after two shakings of *c*, the reaction is ended. The cup *k* should be just deep enough to easily hold the substance: it is desirable to have cups of different sizes to correspond to the volume of the material to be analysed.

When the evolution of gas is complete, *c* is connected with the gas burette, which is filled with mercury, and which has been previously moistened

with a very little water. The nitric oxide is then drawn into the burette by opening *o*, *i*, and *d*, and raising the bulb *e*. The gas is then measured in the usual manner, with allowance for the tension of the water vapour, and the calculation is made.

To clean the apparatus, drive as much of the mercury as possible back into the bulb *e*, close *o*, and open the cylinder *c* over a large beaker of water so as to catch the mercury, and at the same time separate it from the sulphuric acid. *c* is rinsed out with water, and after drying the weighing tube *k*, the apparatus is ready for a new determination. If the warming of the gas burette with the hands has been avoided, the measurement can be made in a very few minutes. The readings are of course very sharp, because there is no sulphuric acid in the gas burette.

To test the purity of the nitric oxide obtained, the gas is led into a double gas pipette containing a solution of a ferrous salt; the evolved carbon dioxide may be absorbed in a pipette containing potassium hydroxide solution.

The analytical absorbing power of a saturated solution of ferrous chloride is 14, of ferrous sulphate 3 to $4\frac{1}{4}$.

To analyse saltpetre in the above apparatus, the substance must first be dissolved in a very little water.

E. B. Hagen has used the apparatus very often for the analysis of gun cotton, and has devised for this purpose a manipulation which admits of very accurate and easy work.

Hagen purposely moistens the vessel *c*, if it is not already sufficiently moist from the preceding analysis. The pressed gun cotton, having been previously finely divided with a knife or rasp, is weighed in the dry

weighing tube *k*, and the apparatus is put together. Before allowing the mercury to enter, *c* is inverted and the contents of the weighing tube fall out and adhere to the moist glass near the stopcock *i*. *c* is then placed in a slanting position, as shown in Fig. 88, and mercury is run in until only a few cubic centimetres of air remain in the cylinder. The tube *x* is now closed air-tight by means of a conical glass rod over which a piece of rubber tubing is drawn. Upon closing the stopcock *o* of the level-bulb the upper part of the apparatus can be exhausted of air more or less thoroughly by sucking upon a tube attached to *i*, either with the mouth or an air-pump. If the stopcock *o* is now opened, mercury enters and completely fills the apparatus. With the ordinary manipulation, air-bubbles might remain enclosed in the gun cotton or fine particles remain in the weighing tube. When the apparatus has thus been made ready, the glass rod is taken out of *x*, sulphuric acid is run in, and the cylinder is heated directly with a Bunsen burner, Fig. 88. When the gun cotton is seen to have dissolved, the apparatus is shaken until no more nitric oxide is given off, and the gas is measured in the manner already described.

Especial attention should be called to the fact that too much sulphuric acid must not be used: 15 ccm. suffices in all cases. On account of the solubility of nitric oxide in sulphuric acid, a correction depending upon the amount of acid used must be brought into the calculation. For 15 ccm. of sulphuric acid 0·21 ccm. is to be considered as having gone into solution. The advantage of the apparatus lies in the great speed with which the work may be done. If the burette stand where the temperature is uniform, and if the

apparatus be brought near the burette only for the purpose of transferring the gas, then two analyses may

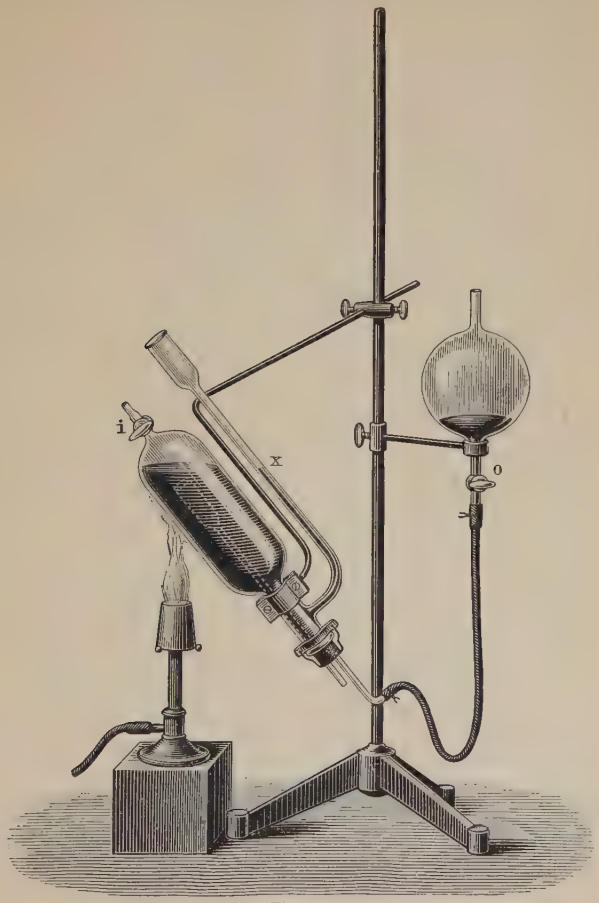

Fig. 88.

easily be made in an hour, since under these circumstances the readings of the gas volumes may be made after ten minutes at the longest.

CHAPTER VII

THE DETERMINATION OF CARBON AND HYDROGEN, AND THE SIMULTANEOUS VOLUMETRIC DETERMINATION OF NITROGEN, IN THE ELEMENTARY ANALYSIS OF ORGANIC SUBSTANCES.

If the combustion of substances containing nitrogen be carried out, not in tubes filled with carbon dioxide or hydrogen, as in the methods of Dumas and Bunsen, but in complete vacuum, it is then possible—provided that after the combustion the tube is again exhausted and the combustion products collected—to weigh the carbon dioxide and water and to measure the nitrogen.

In addition to a combustion furnace, a tube filled with copper oxide, metallic copper, and the substance to be analysed, and absorption apparatus for carbon dioxide and water, the method to be described calls for an air-pump and a graduated tube for measuring the nitrogen.

An operation of this kind can never be carried out with the air-pumps ordinarily in use in laboratories; but it can easily be performed with the air-pump of Professor Töpler, which possesses no stopcocks, no valves, and no dead space.

This air-pump is a combination of three barometers, two of which act as valves, while the third, analogous to the Geissler pump, ends in a thick-walled bulb by means of which the vacuum is produced. The arrangement is shown in Fig. 89.

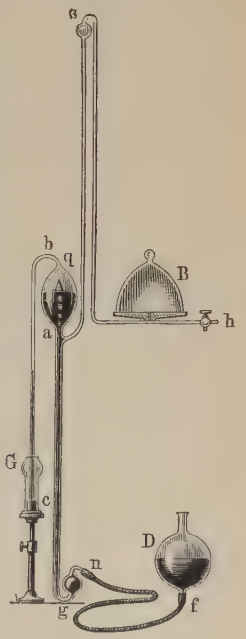

Fig. 89.

In the drawing, *g a* is a wide glass tube ending in the glass bulb *A*, and joined by a wide rubber tube *n f* with the large bulb *D*. From the upper end of *A* a narrow bent tube *q b c* passes downwards into *G*. The length of this last-named tube, from the highest point *b* to the open end *c*, is somewhat more than the greatest barometric height of the locality.

From just below the bulb *A* rises the small tube *a s*, whose highest point is considerably more than the barometric height above the highest point of the tube *q b c*. At *s* this tube bends downward again and is permanently connected with the receiver *B*. The whole system of tubes from *g* to *s* can easily be put together by a glassworker; it is fastened to a suitable wooden standard, which is provided at different levels with supports for the mercury reservoir *D*, so that *D* can easily be brought into any desired position.

D is filled with mercury, and so much mercury is poured into *G* that the end of *b c* is about 1 cm.

below the surface. The apparatus is then ready for use.

Regarding the use of the apparatus, a discrimination must be made between two distinct manipulations:—

1. If D be raised to the height of the bulb A, the air in the latter will be driven out by the mercury, and will escape in a rapid stream of bubbles through the mercury in G. By raising D the mercury in A is brought to the point q. When no more bubbles escape at c, D is brought into its lowest position, as shown in Fig. 89. The mercury in A sinks rapidly and bubbles of air enter from a and rise through A. When the mercury in $a\ g$ has sunk below the point a, the air in B is expanded to the volume $A + B$.

At the same time the mercury in the vessel G, which excludes the outer air, rises slowly in the tube $b\ c$ to a height which corresponds to the difference of pressure. By again raising D the air which has passed from B into A can be driven out at c, the opening a being meanwhile closed by the mercury rising toward A. The pressure in A increases, the mercury in $b\ c$ falling rapidly, while that in $a\ s$ rises above the level in A. It is obvious that the sum of the two columns of mercury in these side barometer tubes is at every moment equal to the difference in pressure between the expanded air in B and the atmosphere.

When the level of the mercury in A has again reached q, the simple operation of raising and lowering D is repeated until no air-bubbles, or only insignificant ones, escape. The apparatus may be compared to the

piston air-pump, if we consider the barometer $A\,g$ with the movable vessel D as the cylinder, the mercury as the piston, and the two barometers $b\,c$ and $a\,s$ as the valves.

In the above manipulation $b\,c$ remains filled after each stroke with air at the pressure of an atmosphere + the small mercury column to be sustained at c. This volume of air, which again expands into A when the mercury is lowered, constitutes, in a manner, the dead space of the air-pump.

2. By a simple modification of the manipulation, the dead space may also be exhausted, after the exhausting in B has gone far enough. To do this, the vessel D, at the end of each stroke, is raised so high that the mercury begins to flow from q through b toward G. If the dimensions of the tube $b\,c$ have been rightly chosen, it fills almost instantly with mercury, the air being completely driven out at c. If D be now brought rapidly into its lowest position, there is formed over the mercury in A a Torricellian vacuum with which the receiver communicates as soon as the mercury has sunk below a. It is clear that by repeating this last proceeding, the exhaustion in B can be carried to any desired limit. At the first stroke thus made bubbles of air are seen to ascend in A from a. This soon ceases, however, if the pumping be continued. The column of mercury in $b\,c$ now stands at the full barometric height during the whole stroke, and only at the moment that the opening a is left free is it possible to discern, from a quick jerk of the mercury in $b\,c$, that a small amount of air has actually passed from B into A. This

jerk becomes steadily weaker and at last imperceptible.

By being repeatedly driven over at b the amount of mercury in D would constantly decrease and would soon stop further exhaustion, unless the mercury in G were poured back into D. Fortunately, however, the apparatus itself relieves the operator of this trouble. If the tube $b\,c$ is only slightly longer than the barometric height, then, when the level in G has been somewhat raised by the overflow of the mercury, the difference of level between G and b will soon become less than the barometric height. Toward the end of the exhausting, a Torricellian vacuum is formed in A at the beginning of every stroke, so that if too much mercury has passed over into G it now flows back of itself into A, and in a short time the level in G is again at the barometric height below b.

If the air is to be completely driven out of $b\,c$, the stream of mercury must hold together and form a column which wholly fills the tube. This result is easily obtained by choosing a tube of not more than 2 to 3 mm. internal diameter, and by avoiding irregular or too sharply curved bends. It is also well to have the tube q widen conically where it joins the bulb A.

It should be noted that after the apparatus has been completely exhausted, the bottle D must be brought to its lowest position before admitting air into the receiver. In other words, the mercury in $a\,g$ should stand below the point a, for otherwise the air entering at h and rushing through B and s would throw any mercury above a with such

force into the empty space A that the bulb might easily be broken.

It is advisable to fasten the air-pump at the points a and n by larger metal bands, the space between the band and the glass being filled with plaster of Paris. The remaining parts of the apparatus should be supported by fairly wide metal bands alone, so as to allow for the different expansion of wood and glass.

It is clear from the description that all of the sources of error introduced by glass stopcocks and greased joints are completely avoided, so that if the receiver B is tight it is impossible for air to enter the apparatus. And further, in the second manner of operating as just described, the layer of air, which in the beginning lies between the mercury and the glass because of the incomplete contact between the last two, is gradually driven out during the exhaustion, so that if the pumping be carried on long enough, there is no limit to the attainable exhaustion of air. Much more perfect exhaustion than is necessary for the analytical methods to be described may easily be obtained with this pump.

To carry out with the aid of this air-pump the simultaneous determination of carbon, hydrogen, and nitrogen, the author has devised the form of apparatus and pump shown in Fig. 90.

A is a small combustion tube, drawn out at one end to a bayonet and at the other to a narrow tube. B is a calcium chloride tube, to the front side of which is fused a small bulb apparatus for holding a few drops of concentrated sulphuric acid. C is a soda-lime tube. D is the air-pump; its escape tube a is bent upward at c in the small mercury trough G, so

that a graduated tube *E* may be brought over its free end. The gases drawn from the apparatus by the pump must then pass into *E* and collect there. The end *c* of the escape tube is fastened into a hollow in

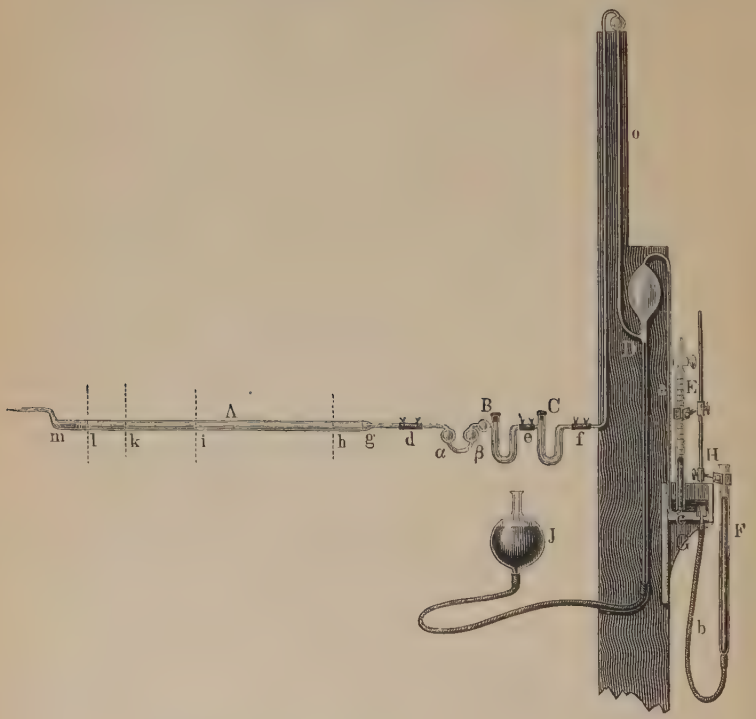

Fig. 90.

the trough by pouring molten sealing-wax around it. The screw-clamp *H* supports the movable tube *F*, which is connected with the trough by the rubber tube *b* wrapped in linen. The apparatus is connected at *d*, *e*, and *f* by pieces of new black rubber tubing supplied with wire ligatures.

The tube *A* is first drawn out at *g* to a thin tube about 7 cm. long. It is then thoroughly dried over a flame, and supplied at *g* with a stopper of ignited long-fibre asbestos. (Short-fibre asbestos might easily be drawn into the calcium chloride tube during the exhaustion.)

The tube is then filled from *g* to *h*—5 to 8 cm.—with copper powder, from *h* to *i*—10 to 40 cm., depending on the nature of the substance to be analysed—with granular copper oxide, from *i* to *k* with a mixture of copper oxide and the substance, and from *k* to *l* with pure copper oxide. At *l* a stopper of freshly ignited asbestos is inserted, and a small platinum boat containing about 0·5 potassium chlorate is pushed in after it. The tube is now drawn out at *m*, in the blast-lamp flame, to a bayonet, the smallest space possible, about 5 cm., being left between *l* and *m*.

The copper powder and copper oxide are brought close together in the tube, and no canal is left, the combustion gases being thus compelled to move through the whole cross-section of the tube.

To prepare the copper powder, coarse-grained sifted copper oxide placed in a small combustion tube is reduced with hydrogen at low red-heat. The reduced copper is then ignited and allowed to cool in a stream of nitrogen. This latter operation is most simply performed by leading 1 to $1\frac{1}{2}$ litres of dry air over the copper immediately after the reduction, and while the tube is still red-hot; in fact it is better to raise the temperature somewhat. The oxygen of the air will oxidise the metallic copper lying next the point of entrance, but the length of the layer thus oxidised

will be less than 5 cm. If the layer of reduced copper oxide is about 15 cm. long, there is thus obtained for the analysis sufficient copper powder which has been ignited in pure nitrogen. The powder is allowed to cool in a slow current of air, the part of the tube where the air enters being kept red-hot for a short time.

The hydrogen used for the reduction must be freed from arsine, stibine, and hydrocarbons by washing it with a solution of potassium permanganate.

Copper powder thus prepared has a beautiful metallic lustre, and repeated experiments have shown that it contains no trace of hydrogen. The formation of carbon monoxide from the carbon dioxide, due to hydrogen in the copper,[1] does not occur here; no water is formed in burning the copper powder to copper oxide. Copper powder made in this manner is an exceptionally good reducing agent, even at a very low red-heat. A close layer 5 to 8 cm. long can with absolute certainty completely decompose, even in a vacuum, the nitric oxide resulting from the combustion of compounds very high in nitrogen. This cannot be done in a vacuum with the ordinary copper spirals.

The grains of sifted copper oxide should be from $1\frac{1}{2}$ to 3 mm. thick. The copper oxide is prepared in the ordinary manner, is freshly ignited before using, and is allowed to cool in a tightly-closed pear-shaped flask with narrow neck.

If the substance to be analysed is a solid, it is shaken from a weighing tube into the combustion

[1] Schrötter and Lautemann.

tube, and is mixed with a copper oxide by means of a bent wire.

To burn liquids of any boiling-point, small bulbs with two capillary side tubes are blown from a thin glass tube (see Fig. 91).

By sucking with the mouth at *c*, there is drawn up into *b* a small amount of an alloy made of 10 parts of

Fig. 91.

Wood's metal (50 parts bismuth, 10 parts cadmium, 27 parts lead, and 13½ parts tin), and 2 to 3 parts mercury. This alloy solidifies at once to a shining and closely adhering thread of metal, without breaking the capillary tube. The melting-point of this alloy lies between 50° and 60° C., quite a little below that of Wood's metal. Moreover, Wood's metal alone breaks the glass walls upon solidifying.

When the glass bulb has been thus prepared, the end *c* is cut off at *d*, and the other end is cut off with

Fig. 92.

the nippers until the thread of metal is from 1 to 2 mm. long. The tube is then filled through *d* (Fig. 92) with the liquid to be analysed, the filling being effected by warming and cooling the bulb in the usual manner. The capillary *e* is then melted together at *d*.

The use of a glass bulb of this form admits of exhausting the combustion tube without loss of the substance by evaporation. The bulb can be opened

when desired by gently warming the end of the capillary containing the alloy. If the substance is very volatile, this capillary is given a length of from 10 to 12 cm., so that when the end is warmed the liquid in the bulb will not be heated to boiling.

The author has found it easily possible with the aid of this bulb to analyse nitrous ether, and can recommend this method of closing the bulb for determinations of vapour density as well as for the ordinary analysis.

In vapour density determinations by Hofmann's method, the metals of Wood's alloy may be disregarded, for the whole metal stopper weighs only 2 to 3 mg. In combustion analyses the mercury is stopped by the wad of asbestos in the end of the combustion tube, if the heat is not raised unnecessarily high.

A small boat about 3 cm. long, made by bending a piece of platinum foil into the desired form, serves to hold the potassium chlorate. It is convenient to measure off the potassium chlorate in a small glass tube closed at one end; the space occupied by 0·5 gram of the finely pulverised salt is noted by a file mark on the outside of the tube.

The potassium chlorate is heated in the platinum boat until it melts, and after solidifying, and while still hot, it is pushed into the combustion tube.

The bayonet of the tube must be drawn out to a very fine point, so that it may be easily broken off inside a rubber tube slipped over it.

The absorption tubes *B* and *C*, Fig. 90 and Fig. 93, are filled with carefully sifted calcium chloride and soda-lime (size of grains, $1\frac{1}{2}$ to 3 mm.), and are closed at *a* with corks and carefully sealed; small bubbles of

air in the sealing-wax may be removed with a hot glass rod. At *b* and *c* (Fig. 93) a little cotton is tightly inserted. These compact stoppers of cotton are sufficiently porous, and the resistance which they offer to the passage of the combustion gases is so great as to render it impossible for the gases to pass through the apparatus too rapidly, and thus escape complete absorption. The U-tubes should be quite small—20 ccm. capacity for each tube is sufficient—and the sulphuric acid in the bulb tube and the soda-lime should be renewed after each analysis. The calcium chloride may be used many times.

After the apparatus has thus been made ready, and

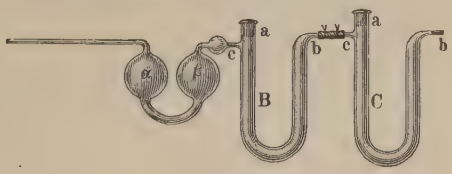

Fig. 93.

the absorption tubes weighed and carefully connected, the combustion is begun by first placing a support under the calcium chloride tube *B* and bringing it into a horizontal position, as shown in Fig. 94. The sulphuric acid in the bulb tube passes into the bulbs *α* and *β*, the air in the combustion tube being thus brought into direct communication with the air-pump. The apparatus is then carefully exhausted. If the capacity of the combustion tube and the absorption apparatus is small in comparison with that of the bulb of the pump, the air may be driven out of the escape tube *a* and the mercury allowed to pass over at the second raising of the mercury reservoir. The

bulb of the air-pump should be of about 500 ccm. capacity, although with a little more time the exhaustion may be made equally well with a smaller bulb. The air-pump used by the author in his experiments had a 150 ccm. bulb made from a large pipette.

Although the tubes are filled with copper oxide, calcium chloride, and soda-lime, the volume of air which they still contain is by no means small. It

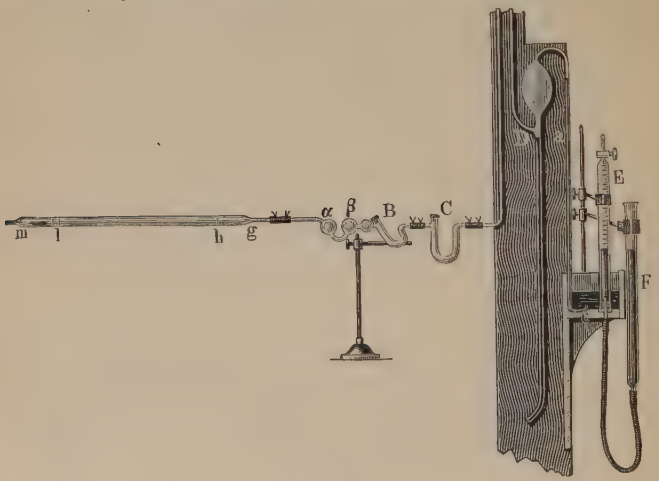

Fig. 94.

amounts to from 100 to 150 ccm., as can easily be shown by placing over *c* in the mercury trough a measuring tube filled with mercury.

When the air in the apparatus is so rarefied that only very small air-bubbles escape through *a*, the combustion tube is heated to glowing at *l*, and the oxygen of the potassium chlorate is thus set free. The oxygen displaces the air in the apparatus and detaches the layer of air adhering to the large surface

of the powdered substances—an operation which many experiments have shown should never be omitted. The apparatus is again exhausted, and when only very small air-bubbles pass over, the copper powder between *g* and *h* is brought to red-heat. The metallic copper unites with the oxygen in the tube, so that, by further pumping, the point is soon reached at which only extremely small bubbles escape through *a*. The apparatus is then sufficiently exhausted; the oxygen remaining in the tubes has no effect upon the accuracy of the results.

The calcium chloride tube is now placed upright, and the substance is burned in the usual manner. It is advisable to lay the combustion tube in a trough consisting of several pieces, and to regulate the heat with small asbestos screens. The tubes can be used several times if the heat rises only to a dark red, this sufficing for complete combustion.

The progress of the combustion may be judged by the rapidity with which the gas passes through the sulphuric acid in the drying tube, and by the heating of the soda-lime tube caused by the absorption of the carbon dioxide; not more than half of the soda-lime tube should become warm.

Small amounts of gas take up a great deal of space in chambers which are nearly exhausted, and for this reason the passage of the gas through the sulphuric acid is at first quite violent. For this reason it is advisable and sometimes necessary, if the substance is not explosive, to close the end *c* of the escape tube *a* during the combustion, and to raise the mercury reservoir *J* (Fig. 90) to the height of the bulb of the air-pump. The pump is thus filled with mercury, and

the evolved gases soon produce a certain pressure within the combustion tube and the absorption apparatus. The amount of this pressure can be told from the position of the mercury in the tube *o*, and can be regulated by raising or lowering the mercury reservoir.

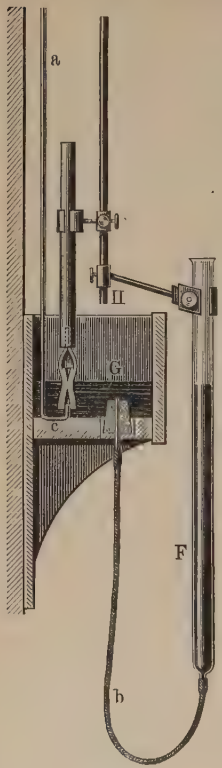

Fig. 95.

The end of *c* is closed with a conical glass tube lined with rubber.[1]

The tube is closed at the upper end and fastened into a wooden rod with sealing-wax. If this cap be pressed down upon the mouth of *c* by means of a clamp, as shown in Fig. 95, the tube is completely closed.

When the combustion is ended the cap is removed, and the graduated tube *E* (Fig. 94) is placed over *c*. *E* must always be moistened near the stopcock with a drop of water. The tube *F* which is connected with the mercury trough by the rubber tube *b* is used for filling the graduated tube. A single-bore rubber stopper fitting the graduated tube is fastened into the bottom of the mercury trough (see Fig. 95) with sealing-wax. The rubber tube *b* is fastened to the glass tube which passes through the stopper. If the graduated tube be pressed down firmly over

[1] Bunsen, *Gasometrische Methoden*, 2d ed. p. 161.

the rubber stopper, it can be easily filled with mercury by raising the tube *F*. And, further, by bringing the tubes *E* and *F* into the position shown in Fig. 94, a gas confined in the measuring tube may be brought under atmospheric pressure and measured, the correction for difference of level of the mercury in tube and trough being thus avoided.

Graduated tubes of this form, supplied with a glass stopcock and holding from 75 to 100 ccm., are very convenient for collecting the gas in the Dumas method for determining nitrogen, or in the Schulze determination of nitric acid; they can easily be filled with sodium hydroxide solution by applying suction at the upper end, and the troublesome inverting of the tubes is thus avoided.

After the combustion, the nitrogen in the tube and the absorption apparatus is drawn over into the graduated tube by means of the air-pump. The exhausting is continued until only extremely small bubbles pass over. It denotes no error if later a passage of gas is shown by a periodic movement of the sulphuric acid in the calcium chloride tube, for this is caused by the small quantity of gas which is still in the tubes and which is disregarded in the analyses. It is advisable to exhaust slowly, for the gases need a certain time to move through the capillary spaces in the asbestos and cotton stoppers.

When the exhausting is ended, *E* is placed as in Fig. 94. A thin rubber tube, which is closed in the middle with a screw pinchcock, is slipped over the bayonet, and the point of the latter is broken off inside of the tube. To burn any carbon which may have separated, dry oxygen is led through

the tube until the metallic copper begins to oxidise. The carbon dioxide and oxygen are then displaced by air; the current of gas can be regulated as desired by raising or lowering the mercury reservoir of the air-pump.

The apparatus is then disconnected, and after it has assumed the temperature of the balance room, it is weighed. The nitrogen is measured and its weight is calculated, with due allowance for temperature, barometric pressure, and the tension of aqueous vapour.

The method takes about as much time as the Dumas determination of nitrogen. It is especially valuable for the analysis of explosive compounds, for the change in pressure causes a change in the boiling-point. For example, nitro-glycerin can be burned and distilled in a vacuum, without explosion resulting; this cannot be done under ordinary atmospheric pressure.

Analyses.

Analysis of Aniline.

	Found.			Calculated.
	I.	II.	III.	
	Per cent.	Per cent.	Per cent.	Per cent.
Carbon . .	77·3	77·9	77·4	77·4
Hydrogen . .	7·6	7·8	8·8 [1]	7·5
Nitrogen . .	14·8	15·0	14·9	15·0
Amount of substance taken	0·2689g.	0·1154g.	0·1089g.	

[1] Asbestos passed over into the calcium chloride tube.

Analysis of Picric Acid.

	Found.			Calculated.
	I.	II.	III.	
	Per cent.	Per cent.	Per cent.	Per cent.
Carbon . .	31·3	31·7	31·1	31·4
Hydrogen . .	2·4[1]	1·6	1·5	1·3
Nitrogen . .	17·9	18·3	18·1	18·3
Amount of substance taken	0·1785g.	0·164g.	0·3333g.	

Analysis of Nitro-Glycerin.

	Found.				Calculated.
	I.	II.	III.	IV.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Carbon .	15·6	15·7	15·7	16·3	15·8
Hydrogen .	2·6	2·9	2·4	2·3	2·2
Nitrogen .	18·5	18·8	18·9	18·7	18·5
Amount of substance taken	0·144g.	0·210g.	0·2803g.	0·3620g.	

If, in pumping out the apparatus, the exhaustion is carried equally far both before and after the combustion, the volumes of gas remaining in the tubes must be in both cases the same, and no errors in the analysis would result, provided that these residual gases had within certain limits the same composition. But at the beginning the combustion tube is filled with air, while, after the combustion, it contains a mixture of water vapour, carbon dioxide, and nitrogen, in which the amount of nitrogen is very small in the greater number of cases. For

[1] See note, p. 348.

this reason the nitrogen result would be too high if the tube were not filled with oxygen as above described, for there remains after the first exhaustion a certain quantity of air, high in nitrogen, which would be displaced by the gases evolved, while after the combustion a gas mixture low in nitrogen results. Aside from the fact that the greatest vacuum possible may be obtained by filling a space with absorbable gases and then absorbing these gases, the errors which might result from incomplete exhaustion are equalised if oxygen is set free as described; for this oxygen cannot escape from the tube, but on the contrary is taken up by the metallic copper.

In the analysis of nitro-glycerin the resulting mixture of water vapour, carbon dioxide, and nitrogen contains a large amount of the last-named substance. For this reason the evolution of oxygen may be omitted if the combustion be made in a short tube about 20 cm. long. Moreover, nitro-glycerin does not evaporate to any extent at ordinary temperatures in a vacuum, so that the substance may be weighed in a boat and mixed directly with the copper oxide. A layer of copper powder about 6 cm. long is brought into the combustion tube, then a layer of copper oxide of about the same length, the boat is introduced, the tube filled with copper oxide and drawn out to a bayonet. The tube is then exhausted as completely as possible and is slowly brought to a red-heat, the heating beginning at the metallic copper. The rest of the operation is like that already described.

Even with a pressure of 290 mm. inside the combustion tube, the nitro-glycerin burned without explosion in my analyses.

CHAPTER VIII

A CALORIMETRIC METHOD FOR THE DETERMINATION OF THE HEATING-POWER OF FUEL

In connection with an extended series of experiments upon the action of furnaces constructed for the smokeless consumption of coal, the author was led to look up the calorimetric determination of the heating-power of fuels. An attempt was first made to work with the calorimeter constructed by F. Fischer, but it was soon found that under the given conditions the determinations could not be carried out with this apparatus. In the investigation in question, the coals were in the form of very fine powder resulting from the taking of an average sample from a large amount of coal (see below).

Although many varied experiments were tried, it was impossible to burn the coal so that, excepting the ash, only gaseous products would result: some tar was always formed. The endeavour to obtain a combustion without the formation of tar, by pressing the coal dust into solid pieces (as later described), and by intermixture of indifferent substances such as in-

fusorial earth, led to no desirable results. Starting with the idea that the preference must be given to that method which would afford a perfectly complete combustion, the author subjected the method of Berthelot[1] to a careful experimental examination, and found that it was actually possible to burn coal with an excess of oxygen and under high pressure, directly to ash, carbon dioxide, water, and nitrogen.

The combustion was made in an autoclave of such a shape that a beaker could be placed inside of it. Beyond this, the manipulation was the same as that described in detail later. The products of combustion were passed first through a calcium chloride tube, and a Liebig potash bulb with caustic potash tube, then through a red-hot tube containing copper oxide, and again through a calcium chloride tube and a Liebig potash bulb with caustic potash tube.

In all cases there was no trace of tar in the beaker within the autoclave; the coal was burned completely, and the ash was fused to a glassy slag. A Saxon coal was used in the experiments.

1. 0·5 gram of coal burned in an autoclave of 300 ccm. capacity, under a pressure of 6 kg. to the square centimetre gave 0·0045 gram carbon dioxide and 0·013 gram water in the incompletely burned products of the combustion.

2. 1 gram of coal burned in an autoclave of 300 ccm. capacity, under a pressure of 8 kg. to the square centimetre, gave 0·105 gram carbon dioxide and 0·0086

[1] *Comptes rendus*, **91**, 188. After devising the method described above, the author became acquainted, through the admirable work of F. Stohmann, Cl. Kleber, and H. Langbein (*Journ. für prakt. Chemie*, 1889, vol. 39, p. 503), with the improvements that had been made meanwhile in the Berthelot method.

gram water in the incompletely burned products of the combustion.

3. 0·779 gram of coal was burned in an autoclave of 260 ccm. capacity, under a pressure of 16 kg. to the square centimetre. The weight of the last potash-bulb was—

Before the experiment, 64·077 grams
After „ „ 64·077 „

4. 0·652 gram of coal was burned in an autoclave of 260 ccm. capacity, under a pressure of 12 kg. to the square centimetre. The weight of the last potash-bulb was—

Before the experiment, 64·077 grams
After „ „ 64·076 „

5. 0·835 gram of coal was burned in an autoclave of 260 ccm. capacity, and under a pressure of 12 kg. to the square centimetre. The weight of the last potash-bulb was—

Before the experiment, 64·076 grams
After „ „ 64·0775 „

6. 0·9878 gram of coal was burned in an autoclave of 260 ccm. capacity, and under a pressure of 12 kg. to the square centimetre. The weight of the last potash-bulb was—

Before the experiment, 64·077 grams
After „ „ 64·077 „

These experiments show that in an apparatus of about $\frac{1}{4}$ litre capacity, 1 gram of coal can be com-

pletely burned in an atmosphere of oxygen under a pressure of 12 kg. to the square centimetre.

It cannot be denied that working with a pressure of several atmospheres entails certain inconveniences. Nevertheless the author is of the opinion that the preference must be given to the Berthelot method above all others, because, on the one hand, the total products of the combustion remain in the calorimeter, thus admitting of a simple and direct measurement of the heat without any calculation, while, on the other hand, complete combustion is attained.

After many unsuccessful experiments, the author has finally succeeded in modifying the Berthelot method so that coal in the form of dust can easily be burned, and he has devised an apparatus with which the experiment can be successfully performed with the aid of simple appliances.

The combustion is made in an apparatus similar to that proposed by Berthelot. The coal is pressed into solid pieces in a steel form[1] by means of an ordinary screw-press, is then electrically ignited, and is burned under a pressure of 12 kg. to the square centimetre (11·6 atmospheres).

The object of the technical examination of coal is to determine the average value of a large mass of fuel, so that to obtain accurate results it is necessary that an average sample be selected with great care. To do this a whole car-load of coal is spread out in a flat heap, and coal is taken out in parallel furrows with a shovel. The coal thus obtained, which should amount to several hectolitres, is broken up to the size

[1] In his calorimetric experiments, Stohmann used solid pieces formed in a similar manner.

of hazel nuts with an ordinary hand stamp, again spread out in a flat heap, and coal is taken from as many different places as possible in the heap until 5 kg. is thus obtained. This 5 kg. is ground to a fine dust in a ball-mill. In this way we get a sample which represents sufficiently well the average composition of the coal in question.

Although it is very convenient, for all other analyses, to have the coal in finely pulverised condition, this is quite undesirable in the calorimetric determination. If we attempt to burn coal-dust in a current of oxygen, the coal-dust lying upon a sheet of asbestos paper, tar is always formed in addition to the gaseous combustion products, if the coal is highly bituminous; in some cases a separation of soot was observed. Moreover, the coal-dust cannot be used direct in the Berthelot apparatus, because the combustion is there made in a basket of platinum wire-gauze.

The difficulty can be avoided very simply by forming the coal-dust into little cylinders by means of high pressure. The arrangement shown in Fig. 96 is used for this purpose. The important portion is the iron form, which is similar to that used by W. Spring in his experiments upon the chemical union of the elements under pressure. This form consists of a screw A, which is bored through and cut in two in the direction of its length, and a nut B by means of which the two halves of A can be held tightly together. The cylindrical punch C, made of hardened steel, fits into the opening of the form. It has been found that all coals which tend to form tar or soot on burning,—in other words, the ordinary bituminous and brown coals,—can be solidified at ordinary temperatures

by high pressure to firm glistening pieces, without the use of any binding material. To facilitate the electrical ignition, a platinum wire about 0·15 to 0·2 mm. diameter and 6 cm. long is pressed into the coal at the beginning. This is done by introducing the wire into the bottom of the cylinder, as shown in Fig. 97,

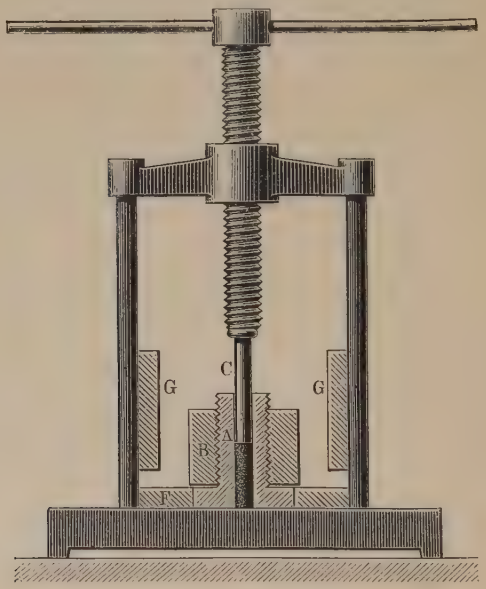

Fig. 96.

which is three times the actual size. The wire is fastened into the holes *e* and the furrows *f* with some wax, and is so bent that it projects upward into the opening of the screw (see Fig. 97).

The form is placed in the press, and about 1·2 grams of coal-dust is poured into the opening. The calculation shows that with an ordinary iron press

a man can easily exert, under the given conditions, a pressure of several thousand atmospheres. The form is held in position during the pressing by inserting the end of it into the hexagonal hole in the plate

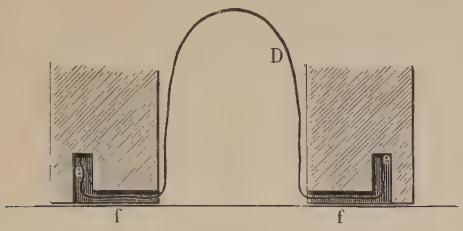

Fig. 97.

F (Fig. 98). Although the pressure may not have been very high, the form is usually forced so tightly into the iron plate that it cannot be drawn out with the hand. It is, however, easily loosened by turning over both form and plate, and laying the plate on the side pieces *G* (Fig. 96). A hexagonal plate is now laid upon the end of the form, and the latter is easily driven out of the plate *F* by turning the screw of the press.

To remove from the form the cylinder of coal produced by the pressure, the nut *B* is unscrewed and the two halves of the screw A are separated. The cylinder of coal usually adheres firmly to one side of *A*. It can easily be removed by carefully loosening it with a small chisel.

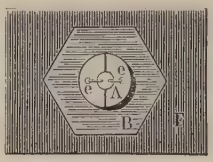

Fig. 98.

In this manner it is possible to form a solid cylinder of coal containing a platinum wire whose free ends project at two points.

After using the form, it is thoroughly cleaned and oiled. The excess of oil is carefully wiped out from the inside of the form before using it again.

All loosely adhering particles are removed from the coal cylinder by gently rubbing it, and pieces are then cut off with a knife until the cylinder weighs about 1 gram. The sample of coal thus prepared is accurately weighed, the weight of the platinum wire being subtracted.

The combustion is carried out in an autoclave of the form shown in Fig. 99 and Fig. 100.[1] This is made from an iron tube, into which a bottom about 15 mm. thick and a top about 30 mm. thick are screwed and fastened with hard solder. The chamber has a capacity of about 250 ccm., and must be tested to a pressure of 25 atmospheres. It is closed by a headpiece whose construction is shown in Fig. 100. This headpiece has a screw valve *a*, an insulated wire *d*, and a perforated clay cup *e*, which is supported by the two platinum wires *ff*. The hole *g* serves as a mercury contact for the other battery wire.

It is very important to obtain good insulation and perfect contact for the wire *d*. To effect this, a conical hole is made through the headpiece, and the upper end of the wire *d* has a conical enlargement *o*. This large end of *d* is inserted into the end of a thin rubber tube, and, by means of a wire attached to its end, the tube is drawn up through the opening in the headpiece. It is self-evident that the contact becomes tighter as the internal pressure increases. It is a mistake to make the area of contact too large,

[1] The iron parts of the apparatus may be obtained from August Kühnscherf und Söhne, Dresden, Germany.

because the pressure then divides itself over the larger face, and consequently will be less upon a unit of surface than if the area of contact is small. For this

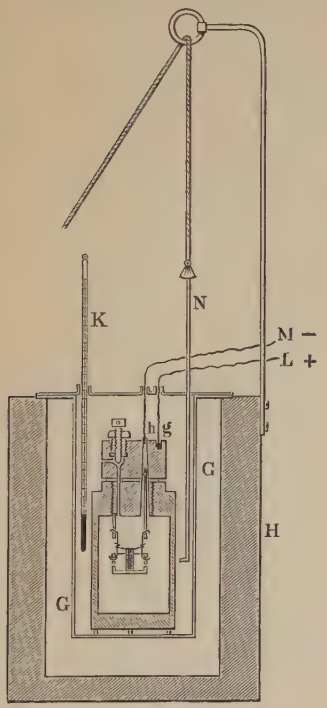

Fig. 99.

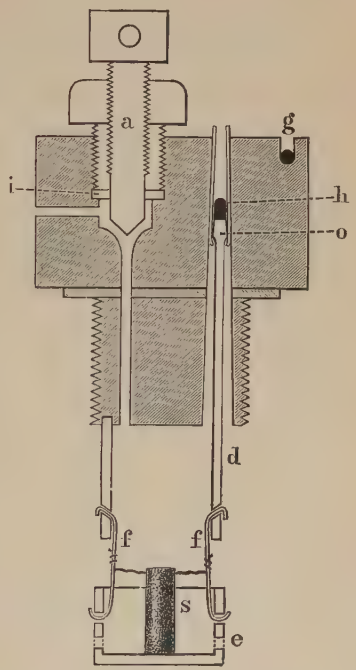

Fig. 100.

reason the surface of contact *o* should not be longer than 5 mm.

The same holds true for the valve, which should press upon a very small surface,—theoretically only a line, because then the pressure would be infinitely great. A lead washer *i* is placed around the valve

rod *a*. It is important that *o* lie high up in the headpiece, so that the rubber will not be attacked during the combustion. The cylinder of coal *s* is placed in the clay cup, and the ends of its platinum wire are wrapped around the platinum wires *ff*.

The apparatus must never be used without first

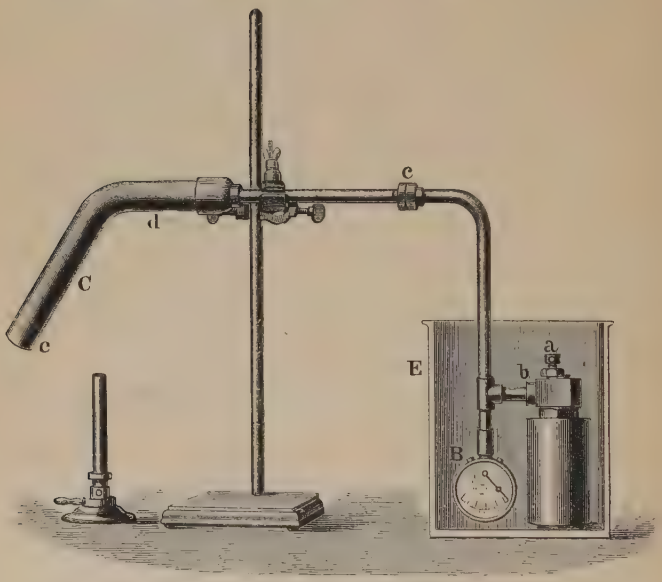

Fig. 101.

assuring one's self that the valve is open and the openings not stopped up.

The headpiece, thus made ready, is screwed firmly into the autoclave, a washer of lead being used to ensure perfect contact.

To fill the autoclave with oxygen, it is joined by the flanges *b* and *c* (Fig. 101) to the oxygen gene-

rator *C*. This tube *C* is an iron pipe of 20 mm. internal diameter. A bottom of wrought-iron is welded into it, and a smaller tube with the flange *c* is fastened into the other end with hard solder.

A manometer *B* is interposed between the autoclave and the retort.

For the sake of safety, the manometer and autoclave stand in a cylinder *E* filled with water and the cylinder is surrounded with a piece of coarse wire-gauze. (This wire-gauze is omitted in the drawing, Fig. 101.)

For generating the oxygen, the tube *C* is filled with 40 grams of a mixture of equal parts of manganese dioxide and potassium chlorate.

C is heated first at *d* with the full flame of a Bunsen burner, and the burner is slowly pushed toward *e*. When the pressure reaches 6 atmospheres the burner is removed, *c* is opened, and the oxygen is allowed to escape until the manometer stands at 0. The flange is then closed again, and by carefully heating the tube *C*, oxygen is evolved until the manometer shows a pressure of 12 kg. to the square centimetre. The valve *a* is then closed, and the autoclave disconnected at *b*. The autoclave is now ready for the calorimetric determination.

Apart from the protection afforded by the cylinder of water *E*, in case of an explosion, it has another great advantage, namely, that the slightest leakage of the autoclave or manometer is shown at once by bubbles of gas escaping and rising through the water.

One should make it a rule to work only with apparatus that is absolutely tight, and new lead washers

should be used whenever the old ones have become worn.

We can never be sure that in the construction of the generator no oil or other organic substance has been introduced; for this reason it is advisable, with a new apparatus, to prepare oxygen once with the flange *c* open. The least trace of oil causes an explosive evolution of gas. In one experiment, the author purposely put some oil into the mixture of manganese dioxide and potassium chlorate, to gain an idea of the consequences of an explosion. It was shown that the arrangement here described afforded sufficient protection. The manometer burst without doing any damage whatever.

It is self-evident that the mixture of manganese dioxide and potassium chlorate must be wholly free from organic substances, sulphur, etc.

The oxygen is given off at temperatures between 210° and 390°; the generator *C* is scarcely attacked at this temperature, and it can be used for hundreds of experiments. The generator is thoroughly cleaned after every determination by boiling it out with water. Direct experiments showed that about 1 ccm. of chlorine is given off with every 1000 ccm. of oxygen. The chlorine is completely removed by inserting into the tube *D* at *c* a close roll of brass wire-gauze. The oxygen, which then passes over into the autoclave, is chemically pure. The wire-gauze is renewed after each experiment.

By the foregoing operation the autoclave is filled with oxygen which is almost absolutely pure.

For the calorimetric measurement, the autoclave is placed in the calorimeter *G* (Fig. 99),

which has been previously filled with 1 litre of water.

The calorimeter consists of a metal vessel *G* supplied with a cover, and hung in a wooden vessel *H*, a space of about 2 cm. existing between *G* and the wood. In the calorimeter is a stirrer *N*, and a fine thermometer *K*, upon which hundredths of a degree can be read. The stirrer consists of a semicircular piece of sheet-iron, and it can be moved up and down by means of two guide rods and a cord which passes through a ring above.

The apparatus is connected with a dip-battery by means of the two wires *L* and *M*, and the mercury contacts *g* and *h*. After the autoclave has been placed in the calorimeter and everything made ready, the apparatus is allowed to stand until the thermometer shows no difference in two readings made five minutes apart. The platinum wire in the coal is then heated to glowing by lowering the battery plates, and the ignition of the coal is thus effected. The water is constantly stirred and the thermometer is watched until the mercury begins to fall again. The temperature at the beginning and the highest temperature at the end are noted.

The calorimetric determination proper takes about 15 minutes; the complete preparation for it can easily be made in an hour.

The heat-capacity of the whole apparatus (autoclave and calorimeter) is best determined by the combustion of carbonised sugar. Such an amount of this sugar-coal is taken that it will give off about the same amount of heat as that produced by 1 gram of average coal.

All errors arising from the radiation of the apparatus, the formation of nitric acid from the nitrogen of the air, etc., are thus made self-compensating in the experiment.

The sugar-coal is prepared by recrystallising the purest commercial sugar several times and igniting it in a refractory crucible in a very hot coke fire. A part of the coal thus obtained is pulverised and mixed with a fourth of its weight of pure sugar. Solid pieces are made from this mixture by putting it into a little cylinder, made by rolling up a piece of platinum foil; the cylinder is then placed in a large platinum crucible, the remaining space in the crucible is filled with sugar-coal, and the whole is heated again for about an hour to strong white heat. The finely powdered coal is cemented together by this coking of the sugar, and when the platinum cylinder is unrolled, the sugar-coal is found to be in the form of a small, glistening, and solid cylinder of coke.

These cylinders cannot be directly ignited by a glowing wire in an atmosphere of oxygen. This ignition is, however, easily brought about by laying a weighed piece of one of the little coal cylinders upon the coke, and igniting this electrically by means of a platinum wire wrapped around it.

It should here be mentioned that the oxygen can of course be driven into the autoclave with a compression pump. Or the compressed oxygen which is supplied in cylinders may be used.

All coal contains sulphur, and hence some sulphurous and sulphuric acid is always formed in the combustion. Experiments showed that, in spite

of this fact, an oxidised apparatus of iron can be used; the heat produced by the action of these acids on the autoclave could not be measured.

For purely scientific work, where the price of the apparatus is of but little importance, and where the highest possible accuracy is to be attained, it would be better to use an autoclave coated on the inside with platinum.

The following examples serve as illustrations of determinations of this kind:—

1. Coal I.—a mixture of brown coal and bituminous coal. Amount taken, 0·9878 gram.

Initial temperature of the calorimeter .	14·19°
Final „ „ .	18·78°

Hence the combustion caused a rise of temperature of 4·59° in the calorimeter, and 1 gram of coal would have caused a rise of temperature of 4·65°.

2. Coal I.—0·835 gram.

Initial temperature . .	13·82°
Final „ . . .	17·7°
Rise of „ . . .	3·88°
„ „ for 1 gram	4·65°

3. Coal I.—0·988 gram.

Initial temperature . .	13·68°
Final „ . . .	18·29°
Rise of „ . . .	4·61°
„ „ for 1 gram	4·66°

4. Coal II.—0·952 gram.

Initial temperature . .	14·62°
Final „ . . .	18·98°

Rise of temperature . .	4·36°
„ „ for 1 gram	4·47°

5. Coal II.—0·992 gram.

Initial temperature . .	14·72°
Final „ . . .	19·3°
Rise of „ . . .	4·58°
„ „ for 1 gram	4·61°

6. Sugar-coal—0·5617 gram.
Coal I.—0·1065 gram.

Initial temperature . .	16·22°
Final „ . . .	20·09°

Rise of temperature of the calorimeter, 3·87°. Since 1 gram of Coal I. gives a rise of temperature of 4·65°, 0·1065 gram will give a rise of 0·49°. Hence the rise of temperature caused by the 0·5617 gram of sugar-coal is 3·38°, and 1 gram of sugar-coal would give 6·01° rise of temperature.

7. Sugar-coal—0·563 gram.
Coal I.—0·174 gram.

Initial temperature . .	15·84°
Final „ . . .	20·02°
Rise of „ . . .	4·18°

Rise of temperature from 0·174 gram of Coal I. is 0·81°. Hence 0·563 gram of sugar-coal causes a rise of 3·37°, and 1 gram of sugar-coal would cause a rise of temperature of 6·00°.

The elementary analysis of the sugar-coal gave—

99·5	per cent	carbon
0·1	„	hydrogen
0·3	„	ash.

If the calorific value of the sugar-coal be taken as 99·5 per cent that of pure carbon, the rise of temperature which 1 gram of chemically pure carbon will produce in the apparatus is found by the proportion—

$$99{\cdot}5 : 100 = 6{\cdot}01 : x,$$
$$x = 6{\cdot}04^{\circ}.$$

Since the absolute heating power of carbon is 8080, the heating power of Coal I. is given by the proportion—

$$6{\cdot}04 : 4{\cdot}65 = 8080 : x,$$
$$x = 6220 \text{ calories.}$$

Coal II.—

$$6{\cdot}04 : 4{\cdot}54 = 8080 : x,$$
$$x = 6072 \text{ calories.}$$

In the practical using of coal the combustion does not take place in closed chambers,—*i.e.* under constant volume,—but under constant pressure, so that, strictly speaking, the values thus found must be somewhat modified. If, however, we remember that in the combustion of pure carbon or pure cellulose, in closed chambers, no change of pressure takes place in the calorimeter, it is seen that this correction may be wholly disregarded in the case of the ordinary moist coals.

For Coal I., for example, the recalculation gave a correction of 6·6 calories, a figure which, even in the most accurate scientific researches, falls wholly within the limits of the unavoidable errors; in fact the latest determinations by Berthelot have given the absolute heating power of amorphous carbon not as 8080, as usually taken, but as 8137·4 calories.

Atomic Weights of the Chemical Elements.

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	27·01	Mercury	Hg	199·71
Antimony	Sb	119·96	Molybdenum	Mo	95·53
Arsenic	As	74·92	Nickel	Ni	57·93
Barium	Ba	136·76	Nitrogen	N	14·021
Beryllium	Be	9·085	Osmium	Os	198·49
Bismuth	Bi	207·52	Oxygen	O	15·963
Boron	B	10·94	Palladium	Pd	105·74
Bromine	Br	79·77	Phosphorus	P	30·96
Cadmium	Cd	111·84	Platinum	Pt	194·415
Caesium	Cs	132·58	Potassium	K	39·02
Calcium	Ca	39·99	Rhodium	Rh	104·06
Carbon	C	11·974	Rubidium	Rb	85·25
Cerium	Ce	140·42	Ruthenium	Ru	104·22
Chlorine	Cl	35·37	Scandium	Sc	43·98
Chromium	Cr	52·01	Selenium	Se	78·80
Cobalt	Co	58·89	Silicon	Si	28·20
Columbium	Cb	93·81	Silver	Ag	107·675
Copper	Cu	63·17	Sodium	Na	22·998
Didymium	Di	144·57	Strontium	Sr	87·37
Erbium	Er	165·89	Sulphur	S	31·984
Fluorine	F	18·98	Tantalum	Ta	182·14
Gallium	Ga	68·85	Tellurium	Te	127·96
Gold	Au	196·16	Thallium	Tl	203·72
Hydrogen	H	1	Thorium	Th	233·41
Indium	In	113·40	Tin	Sn	117·70
Iodine	I	126·56	Titanium	Ti	49·85
Iridium	Ir	192·65	Tungsten	W	183·61
Iron	Fe	55·91	Uranium	U	238·48
Lanthanum	La	138·53	Vanadium	V	51·26
Lead	Pb	206·47	Ytterbium	Yb	172·76
Lithium	Li	7·007	Yttrium	Y	89·82
Magnesium	Mg	23·96	Zinc	Zn	64·90
Manganese	Mn	53·91	Zirconium	Zr	89·37

The following tables are taken from the *Physikalisch-chemische Tabellen* by Landolt and Börnstein, and are here inserted by permission of Professor Dr. H. Landolt.—*Translator.*

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0{\cdot}003670t)$ for $t = -2$ to $+4°$.

If V is the volume of a gas at $t°$ and h mm. pressure of mercury, then at 0° and 760 mm. pressure the volume $V_0 = \frac{V}{1 + 0{\cdot}003670t} \frac{h}{760}$.

t	$1+0{\cdot}003670t$	$\text{Log}\frac{1}{1+0{\cdot}003670t}$	t	$1+0{\cdot}003670t$	$\text{Log}\frac{1}{1+0{\cdot}003670t}$
	0,	0,		1,	9, −10
−2°·0	99266	00320	1°·1	00404	99825
−1·9	99303	00304	1·2	00440	99809
−1·8	99339	00288	1·3	00477	99793
−1·7	99376	00272	1·4	00514	99777
−1·6	99413	00256	1·5	00551	99761
−1·5	99449	00240	1·6	00587	99746
−1·4	99486	00224	1·7	00624	99730
−1·3	99523	00208	1·8	00661	99714
−1·2	99560	00192	1·9	00697	99698
−1·1	99596	00176	2·0	00734	99682
−1·0	99633	00160		1,	9, −10
	0,	0,	2·1	00771	99666
−0·9	99670	00144	2·2	00807	99651
−0·8	99706	00128	2·3	00844	99635
−0·7	99743	00112	2·4	00881	99619
−0·6	99780	00096	2·5	00918	99603
−0·5	99816	00080	2·6	00954	99588
−0·4	99853	00064	2·7	00991	99572
−0·3	99890	00048	2·8	01028	99556
−0·2	99927	00032	2·9	01064	99540
−0·1	99963	00016	3·0	01101	99524
0·0	100000	00000		1,	9, −10
	1,	9, −10	3·1	01138	99509
+0·1	00037	99984	3·2	01174	99493
0·2	00073	99968	3·3	01211	99477
0·3	00110	99952	3·4	01248	99461
0·4	00147	99936	3·5	01285	99445
0·5	00184	99920	3·6	01321	99430
0·6	00220	99905	3·7	01358	99414
0·7	00257	99889	3·8	01395	99398
0·8	00294	99873	3·9	01431	99383
0·9	00330	99857	4·0	01468	99367
1·0	00367	99841			

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0{\cdot}003670t)$ for $t = 4{\cdot}1$ to $14{\cdot}0°$.

t	$1+0{\cdot}003670t$	$\text{Log}\frac{1}{1+0{\cdot}003670t}$	t	$1+0{\cdot}003670t$	$\text{Log}\frac{1}{1+0{\cdot}003670t}$
	1,	9, −10		1,	9, −10
4°·1	01505	99351	9°·1	03340	98573
4·2	01541	99336	9·2	03376	98558
4·3	01578	99320	9·3	03413	98542
4·4	01615	99304	9·4	03450	98527
4·5	01652	99288	9·5	03487	98511
4·6	01688	99273	9·6	03523	98496
4·7	01725	99257	9·7	03560	98481
4·8	01762	99241	9·8	03597	98465
4·9	01798	99226	9·9	03633	98450
5·0	01835	99210	10·0	03670	98435
	1,	9, −10		1,	9, −10
5·1	01872	99195	10·1	03707	98420
5·2	01908	99179	10·2	03743	98404
5·3	01945	99163	10·3	03780	98389
5·4	01982	99148	10·4	03817	98373
5·5	02019	99132	10·5	03854	98358
5·6	02055	99117	10·6	03890	98343
5·7	02092	99101	10·7	03927	98327
5·8	02129	99085	10·8	03964	98312
5·9	02165	99070	10·9	04000	98297
6·0	02202	99054	11·0	04037	98281
	1,	9, −10		1,	9, −10
6·1	02239	99038	11·1	04074	98266
6·2	02275	99023	11·2	04110	98251
6·3	02312	99007	11·3	04147	98235
6·4	02349	98992	11·4	04184	98220
6·5	02386	98976	11·5	04221	98204
6·6	02422	98961	11·6	04257	98189
6·7	02459	98945	11·7	04294	98174
6·8	02496	98929	11·8	04331	98159
6·9	02532	98914	11·9	04367	98144
7·0	02569	98899	12·0	04404	98128
	1,	9, −10		1,	9, −10
7·1	02606	98883	12·1	04441	98113
7·2	02642	98867	12·2	04477	98098
7·3	02679	98852	12·3	04514	98083
7·4	02716	98836	12·4	04551	98067
7·5	02753	98821	12·5	04588	98052
7·6	02789	98805	12·6	04624	98037
7·7	02826	98790	12·7	04661	98022
7·8	02863	98774	12·8	04698	98006
7·9	02899	98759	12·9	04734	97991
8·0	02936	98743	13·0	04771	97976
	1,	9, −10		1,	9, −10
8·1	02973	98728	13·1	04808	97961
8·2	03009	98712	13·2	04844	97945
8·3	03046	98697	13·3	04881	97930
8·4	03083	98681	13·4	04918	97915
8·5	03120	98666	13·5	04955	97900
8·6	03156	98651	13·6	04991	97885
8·7	03193	98635	13·7	05028	97869
8·8	03230	98619	13·8	05065	97854
8·9	03266	98604	13·9	05101	97839
9·0	03303	98589	14·0	05138	97824

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0{\cdot}003670t)$ for $t = 14{\cdot}1$ to $24{\cdot}0°$.

t	$1+0{\cdot}003670t$	$\text{Log}\frac{1}{1+0{\cdot}003670t}$	t	$1+0{\cdot}003670t$	$\text{Log}\frac{1}{1+0{\cdot}003670t}$
	1,	9, −10		1,	9, −10
14°·1	05175	97809	19°·1	07010	97058
14·2	05211	97794	19·2	07046	97043
14·3	05248	97779	19·3	07083	97028
14·4	05285	97763	19·4	07120	97013
14·5	05322	97748	19·5	07157	96998
14·6	05358	97733	19·6	07193	96983
14·7	05395	97718	19·7	07230	96968
14·8	05432	97703	19·8	07267	96954
14·9	05468	97688	19·9	07303	96939
15·0	05505	97673	20·0	07340	96924
	1,	9, −10		1,	9, −10
15·1	05542	97657	20·1	07377	96909
15·2	05578	97642	20·2	07413	96894
15·3	05615	97627	20·3	07450	96879
15·4	05652	97612	20·4	07487	96864
15·5	05689	97597	20·5	07524	96850
15·6	05725	97582	20·6	07560	96835
15·7	05762	97567	20·7	07597	96820
15·8	05799	97552	20·8	07634	96805
15·9	05835	97537	20·9	07670	96791
16·0	05872	97522	21·0	07707	96776
	1,	9, −10		1,	9, −10
16·1	05909	97507	21·1	07744	96761
16·2	05945	97492	21·2	07780	96746
16·3	05982	97477	21·3	07817	96731
16·4	06019	97462	21·4	07854	96716
16·5	06056	97447	21·5	07891	96702
16·6	06092	97432	21·6	07927	96687
16·7	06129	97417	21·7	07964	96672
16·8	06166	97402	21·8	08001	96657
16·9	06202	97387	21·9	08037	96643
17·0	06239	97372	22·0	08074	96628
	1,	9, −10		1,	9, −10
17·1	06276	97357	22·1	08111	96613
17·2	06312	97342	22·2	08147	96598
17·3	06349	97327	22·3	08184	96584
17·4	06386	97312	22·4	08221	96569
17·5	06423	97297	22·5	08258	96554
17·6	06459	97282	22·6	08294	96539
17·7	06496	97267	22·7	08331	96525
17·8	06533	97252	22·8	08368	96510
17·9	06569	97237	22·9	08404	96495
18·0	06606	97222	23·0	08441	96481
	1,	9, −10		1,	9, −10
18·1	06643	97207	23·1	08478	96466
18·2	06679	97192	23·2	08514	96451
18·3	06716	97177	23·3	08551	96437
18·4	06753	97162	23·4	08588	96422
18·5	06790	97147	23·5	08625	96407
18·6	06826	97132	23·6	08661	96393
18·7	06863	97117	23·7	08698	96378
18·8	06900	97102	23·8	08735	96363
18·9	06936	97088	23·9	08771	96349
19·0	06973	97073	24·0	08808	96334

Value of $(1 + 0{\cdot}003670t)$ for $t = 24{\cdot}1$ to $34{\cdot}0°$.

t	$1+0{\cdot}003670t$	$\text{Log}\frac{1}{1+0{\cdot}003670t}$	t	$1+0{\cdot}003670t$	$\text{Log}\frac{1}{1+0{\cdot}003670t}$
	1,	9, −10		1,	9, −10
24°·1	08845	96319	29°·1	10680	95593
24·2	08881	96305	29·2	10716	95579
24·3	08918	96290	29·3	10753	95565
24·4	08955	96275	29·4	10790	95550
24·5	08992	96261	29·5	10827	95535
24·6	09028	96246	29·6	10863	95521
24·7	09065	96231	29·7	10900	95507
24·8	09102	96217	29·8	10937	95492
24·9	09138	96202	29·9	10973	95478
25·0	09175	96188	30·0	11010	95464
	1,	9, −10		1,	9, −10
25·1	09212	96173	30·1	11047	95449
25·2	09248	96159	30·2	11083	95435
25·3	09285	96144	30·3	11120	95421
25·4	09322	96129	30·4	11157	95406
25·5	09359	96115	30·5	11194	95392
25·6	09395	96100	30·6	11230	95378
25·7	09432	96086	30·7	11267	95363
25·8	09469	96071	30·8	11304	95349
25·9	09505	96057	30·9	11340	95335
26·0	09542	96042	31·0	11377	95320
	1,	9, −10		1,	9, −10
26·1	09579	96027	31·1	11414	95306
26·2	09615	96013	31·2	11450	95292
26·3	09652	95998	31·3	11487	95278
26·4	09689	95984	31·4	11524	95263
26·5	09726	95969	31·5	11561	95249
26·6	09762	95955	31·6	11597	95235
26·7	09799	95940	31·7	11634	95220
26·8	09836	95925	31·8	11671	95206
26·9	09872	95901	31·9	11707	95192
27·0	09909	95897	32·0	11744	95178
	1,	9, −10		1,	9, −10
27·1	09946	95882	32·1	11781	95163
27·2	09982	95868	32·2	11817	95149
27·3	10019	95853	32·3	11854	95135
27·4	10056	95839	32·4	11891	95120
27·5	10093	95824	32·5	11928	95106
27·6	10129	95810	32·6	11964	95092
27·7	10166	95795	32·7	12001	95078
27·8	10203	95781	32·8	12038	95064
27·9	10239	95767	32·9	12074	95049
28·0	10276	95752	33·0	12111	95035
	1,	9, −10		1,	9, −10
28·1	10313	95737	33·1	12148	95021
28·2	10349	95723	33·2	12184	95007
28·3	10386	95709	33·3	12221	94993
28·4	10423	95694	33·4	12258	94978
28·5	10460	95679	33·5	12295	94964
28·6	10496	95665	33·6	12331	94950
28·7	10533	95651	33·7	12368	94936
28·8	10570	95636	33·8	12405	94922
28·9	10606	95622	33·9	12441	94907
29·0	10643	95608	34·0	12478	94893

Tension of Aqueous Vapour

Expressed in millimetres of mercury at 0°, *density of mercury* = 13·59593 *at latitude* 45° *and at the sea-level.*

Calculated from Regnault's measurements by Broch (*Trav. et Mém. du Bur. intern. des Poids et Mes.* I A. 33, 1881).

t	Tension	t	Tension	t	Tension	t	Tension
	mm.		mm.		mm.		mm.
−2°·0	3·9499	2°·6	5·5008	7°·1	7·5171	11°·6	10·1614
−1·9	3·9790	2·7	5·5398	7·2	7·5685	11·7	10·2285
−1·8	4·0082	2·8	5·5790	7·3	7·6202	11·8	10·2960
−1·7	4·0376	2·9	5·6185	7·4	7·6722	11·9	10·3639
−1·6	4·0672	3·0	5·6582	7·5	7·7246	12·0	10·4322
−1·5	4·0970			7·6	7·7772		
−1·4	4·1271	3·1	5·6981	7·7	7·8302	12·1	10·5009
−1·3	4·1574	3·2	5·7383	7·8	7·8834	12·2	10·5700
−1·2	4·1878	3·3	5·7788	7·9	7·9370	12·3	10·6394
−1·1	4·2185	3·4	5·8195	8·0	7·9909	12·4	10·7093
		3·5	5·8605			12·5	10·7796
−1·0	4·2493	3·6	5·9017	8·1	8·0452	12·6	10·8503
−0·9	4·2803	3·7	5·9432	8·2	8·0998	12·7	10·9214
−0·8	4·3116	3·8	5·9850	8·3	8·1547	12·8	10·9928
−0·7	4·3430	3·9	6·0270	8·4	8·2099	12·9	11·0647
−0·6	4·3747	4·0	6·0693	8·5	8·2655	13·0	11·1370
−0·5	4·4065			8·6	8·3214		
−0·4	4·4385	4·1	6·1118	8·7	8·3777	13·1	11·2097
−0·3	4·4708	4·2	6·1546	8·8	8·4342	13·2	11·2829
−0·2	4·5032	4·3	6·1977	8·9	8·4911	13·3	11·3564
−0·1	4·5359	4·4	6·2410	9·0	8·5484	13·4	11·4304
		4·5	6·2846			13·5	11·5048
0·0	4·5687	4·6	6·3285			13·6	11·5797
+0·1	4·6017	4·7	6·3727	9·1	8·6061	13·7	11·6550
0·2	4·6350	4·8	6·4171	9·2	8·6641	13·8	11·7307
0·3	4·6685	4·9	6·4618	9·3	8·7224	13·9	11·8069
0·4	4·7022	5·0	6·5067	9·4	8·7810	14·0	11·8835
0·5	4·7361			9·5	8·8400		
0·6	4·7703			9·6	8·8993		
0·7	4·8047	5·1	6·5519	9·7	8·9589	14·1	11·9605
0·8	4·8393	5·2	6·5974	9·8	9·0189	14·2	12·0380
0·9	4·8741	5·3	6·6432	9·9	9·0792	14·3	12·1159
1·0	4·9091	5·4	6·6893	10·0	9·1398	14·4	12·1943
		5·5	6·7357			14·5	12·2731
1·1	4·9443	5·6	6·7824	10·1	9·2009	14·6	12·3523
1·2	4·9798	5·7	6·8293	10·2	9·2623	14·7	12·4320
1·3	5·0155	5·8	6·8765	10·3	9·3241	14·8	12·5122
1·4	5·0515	5·9	6·9240	10·4	9·3863	14·9	12·5928
1·5	5·0877	6·0	6·9718	10·5	9·4488	15·0	12·6739
1·6	5·1240			10·6	9·5117		
1·7	5·1606	6·1	7·0198	10·7	9·5750	15·1	12·7554
1·8	5·1975	6·2	7·0682	10·8	9·6387	15·2	12·8374
1·9	5·2346	6·3	7·1168	10·9	9·7027	15·3	12·9198
2·0	5·2719	6·4	7·1658	11·0	9·7671	15·4	13·0027
		6·5	7·2150			15·5	13·0861
2·1	5·3094	6·6	7·2646	11·1	9·8318	15·6	13·1700
2·2	5·3472	6·7	7·3145	11·2	9·8969	15·7	13·2543
2·3	5·3852	6·8	7·3647	11·3	9·9624	15·8	13·3392
2·4	5·4235	6·9	7·4152	11·4	10·0283	15·9	13·4245
2·5	5·4620	7·0	7·4660	11·5	10·0946	16·0	13·5103

Tension of Aqueous Vapour—*Continued.*

t	Tension	t	Tension	t	Tension	t	Tension
	mm.		mm.		mm.		mm.
16°·1	13·5965	20°·6	18·0176	25·1	23·6579	29°·6	30·7928
16·2	13·6832	20·7	18·1288	25·2	23·7991	29·7	30·9707
16·3	13·7705	20·8	18·2406	25·3	23·9411	29·8	31·1494
16·4	13·8582	20·9	18·3529	25·4	24·0838	29·9	31·3291
16·5	13·9464	21·0	18·4659	25·5	24·2272	30·0	31·5096
16·6	14·0351			25·6	24·3714		
16·7	14·1243	21·1	18·5795	25·7	24·5164	30·1	31·6910
16·8	14·2141	21·2	18·6937	25·8	24·6620	30·2	31·8734
16·9	14·3043	21·3	18·8085	25·9	24·8084	30·3	32·0567
17·0	14·3950	21·4	18·9240	26·0	24·9556	30·4	32·2410
		21·5	19·0400			30·5	32·4262
17·1	14·4862	21·6	19·1567	26·1	25·1035	30·6	32·6124
17·2	14·5779	21·7	19·2740	26·2	25·2523	30·7	32·7995
17·3	14·6702	21·8	19·3920	26·3	25·4018	30·8	32·9875
17·4	14·7630	21·9	19·5105	26·4	25·5521	30·9	33·1765
17·5	14·8563	22·0	19·6297	26·5	25·7032	31·0	33·3664
17·6	14·9501			26·6	25·8551		
17·7	15·0444	22·1	19·7496	26·7	26·0077	31·1	33·5573
17·8	15·1392	22·2	19·8701	26·8	26·1612	31·2	33·7491
17·9	15·2345	22·3	19·9912	26·9	26·3155	31·3	33·9419
18·0	15·3304	22·4	20·1130	27·0	26·4705	31·4	34·1356
		22·5	20·2355			31·5	34·3303
18·1	15·4268	22·6	20·3586	27·1	26·6263	31·6	34·5259
18·2	15·5237	22·7	20·4824	27·2	26·7830	31·7	34·7225
18·3	15·6212	22·8	20·6068	27·3	26·9405	31·8	34·9201
18·4	15·7192	22·9	20·7319	27·4	27·0987	31·9	35·1186
18·5	15·8178	23·0	20·8576	27·5	27·2578	32·0	35·3181
18·6	15·9169			27·6	27·4177		
18·7	16·0166	23·1	20·9840	27·7	27·5784	32·1	35·5186
18·8	16·1168	23·2	21·1110	27·8	27·7399	32·2	35·7201
18·9	16·2176	23·3	21·2388	27·9	27·9023	32·3	35·9226
19·0	16·3189	23·4	21·3672	28·0	28·0654	32·4	36·1261
		23·5	21·4964			32·5	36·3307
19·1	16·4208	23·6	21·6262	28·1	28·2294	32·6	36·5363
19·2	16·5233	23·7	21·7567	28·2	28·3942	32·7	36·7429
19·3	16·6263	23·8	21·8879	28·3	28·5599	32·8	36·9505
19·4	16·7299	23·9	22·0198	28·4	28·7265	32·9	37·1592
19·5	16·8341	24·0	22·1524	28·5	28·8939	33·0	37·3689
19·6	16·9388			28·6	29·0622		
19·7	17·0441	24·1	22·2857	28·7	29·2313	33·1	37·5796
19·8	17·1499	24·2	22·4196	28·8	29·4013	33·2	37·7914
19·9	17·2563	24·3	22·5543	28·9	29·5722	33·3	38·0042
20·0	17·3632	24·4	22·6898	29·0	29·7439	33·4	38·2180
		24·5	22·8259			33·5	38·4329
20·1	17·4707	24·6	22·9628	29·1	29·9165	33·6	38·6488
20·2	17·5789	24·7	23·1003	29·2	30·0900	33·7	38·8657
20·3	17·6877	24·8	23·2386	29·3	30·2644	33·8	39·0837
20·4	17·7971	24·9	23·3777	29·4	30·4396	33·9	39·3027
20·5	17·9071	25·0	23·5174	29·5	30·6157	34·0	39·5228

Theoretical Densities of Gases

And weights of one litre of the same at 0° and 760 mm. pressure, for latitude 45° and that of Berlin.

Substance.	Formula.	Density.		Weight of 1 litre in grams.	
		Hydrogen = 2. (Mol. Wt.)	Air = 1.	Latitude 45° at sea-level.	In Berlin.
Acetylene	C_2H_2	25·947	0·89820	1·16143	1·16219
Allylene	C_3H_4	39·921	1·38194	1·78692	1·78811
Ammonia	NH_3	17·012	0·58890	0·76148	0·76199
Arsine	AsH_3	77·918	2·69728	3·48772	3·49003
Bromine	Br_2	159·538	5·52271	7·14115	7·14588
Butane	C_4H_{10}	57·894	2·00411	2·59142	2·59314
Butylene	C_4H_8	55·894	1·93488	2·50190	2·50355
Carbon dioxide	CO_2	43·900	1·51968	1·96503	1·96633
Carbon monoxide	CO	27·937	0·96709	1·25050	1·25133
Carbon oxysulphide	COS	59·937	2·07483	2·68287	2·68464
Carbonyl chloride	$COCl_2$	98·689	3·41631	4·41746	4·42039
Chlorine	Cl_2	70·752	2·44921	3·16696	3·16906
Cyanogen	C_2N_2	51·971	1·79907	2·32630	2·32784
Ethane	C_2H_6	29·947	1·03667	1·34047	1·34136
Ethylene	C_2H_4	27·947	0·96744	1·25095	1·25178
Hydriodic acid	HI	127·559	4·41570	5·70972	5·71351
Hydrobromic acid	HBr	80·769	2·79597	3·61534	3·61773
Hydrochloric acid	HCl	36·376	1·25922	1·62824	1·62932
Hydrofluoric acid	HF	19·984	0·69178	0·89451	0·89511
Hydrogen	H_2	2·000	0·069234	0·089523	0·089582
Hydrogen selenide	H_2Se	80·797	2·79694	3·61659	3·61899
Hydrogen sulphide	H_2S	34·000	1·17697	1·52189	1·52290
Hydrogen telluride	H_2Te	129·960	4·49881	5·81720	5·82105
Methane	CH_4	15·974	0·55297	0·71502	0·71549
Nitric oxide	NO	29·975	1·03764	1·34172	1·34261
Nitrogen	N_2	28·024	0·97010	1·25440	1·25523
Nitrous oxide	N_2O	43·987	1·52269	1·96892	1·97023
Oxygen	O_2	31·927	1·10521	1·42908	1·43003
Phosphine	PH_3	33·958	1·17552	1·52001	1·52102
Propane	C_3H_8	43·921	1·52041	1·96597	1·96727
Propylene	C_3H_6	41·921	1·45118	1·87644	1·87769
Silicon tetrafluoride	SiF_4	104·131	3·60469	4·66105	4·66414
Sulphur dioxide	SO_2	63·927	2·21295	2·86146	2·86336
Water vapour	H_2O	17·963	0·62182	0·80405	0·80458
Atmospheric air	...	...	1·00000	1·293052	1·293909

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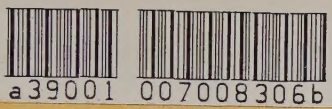
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